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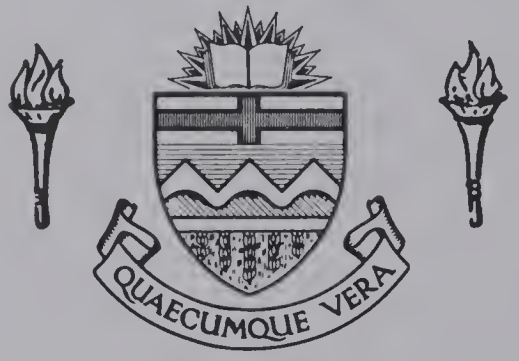

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EXTRACTION OF VANADIUM FROM OIL SANDS FLY ASH

by

LINDA G. SCHNEIDER

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled EXTRACTION OF VANADIUM FROM OIL SANDS FLY ASH submitted by LINDA G. SCHNEIDER in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE in METALLURGY.

ABSTRACT

Vanadium is a potentially important by-product of the petroleum recovery operations from Athabasca oil sands. The production from the current throughput of the Suncor and Syncrude plants would yield 2000 tonnes/year of vanadium pentoxide, or about 12% of the total western world production in 1980. Although bitumen contains only 200 ppm vanadium, the vanadium concentrates in the coke during upgrading and reaches a concentration of 2 to 3% (carbon-free basis) in the fly ash produced from combustion of the coke. A process is described in which 88% of the vanadium was recovered from Suncor fly ash. Carbon-free fly ash was roasted with 25% sodium chloride at 850°C for 4 hr to convert the vanadium to water-soluble sodium vanadate which was subsequently extracted by leaching with hot water. The effects of various process conditions on the production of water-soluble sodium vanadate were studied. Unburned carbon in the fly ash, moisture in the roast atmosphere, and excessive gas/solid contact were particularly detrimental. The leachate contained 32 g/l vanadium pentoxide equivalent, 27 g/l sodium, 11 g/l sulfate, and 0.7 g/l calcium. Nickel, iron, aluminum and silicon were present at concentrations of 0.1 g/l or less. Vanadium was precipitated from the leachate as ammonium metavanadate by adjusting the pH to 11, filtering the impurities that precipitated, and adding ammonium chloride crystals to the clarified leachate to a concentration of 1.4M. The ammonium metavanadate that

precipitated contained 0.10% sodium, with calcium, sulfur, silicon, aluminum, nickel, and iron present at concentrations of less than 0.06%.

Recovery of vanadium from the fly ash is dependent upon combustion of the oil sands coke. The coke contains 6 to 8% sulfur, with the consequence that only part of the coke production can be burned because of government regulations restricting sulfur dioxide emissions. Included in this study is the extraction of vanadium from the ash of a low-sulfur-emission coke which was produced in the laboratory by addition of calcium hydroxide to Athabasca bitumen prior to coking. Although the vanadium (and nickel) could be readily leached from the ash by acid leachates, excessive amounts of acid were consumed by basic compounds in the ash. The leachate contained only 1.2 g/l vanadium pentoxide and many acid soluble impurities, necessitating the use of solvent extraction for the purification and recovery of vanadium from the leachate. Also, an unfilterable precipitate formed during the pH adjustment of the leachate required for solvent extraction of vanadium from the leachate. The vanadium could also be leached with a sodium carbonate solution but excessive amounts of sodium carbonate were required.

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I. INTRODUCTION

Vanadium is an important industrial metal used mainly as an alloying agent in iron and steel. Although Canada currently has no domestic production of vanadium and imports its requirements from the United States, Canada's potential domestic sources consist of fly ash produced by the Athabasca Oil Sands petroleum recovery plants, the titaniferous magnetites of Quebec, and fly ash derived through refining imported vanadium-containing crude oils (1).

The recovery of vanadium from Quebec titaniferous magnetites (0.19% V) has been investigated in laboratory (2) and pilot plant studies (3). If these titaniferous magnetites are commercially developed for iron production, the production of vanadium as a by-product may be feasible.

The recovery of vanadium from fly ash derived through refining Venezuelan crude was shown to be commercially feasible by Canadian Petrofina in the early 1970s (4). However, the vanadium recovery operations ceased when the refinery switched to an alternate, vanadium-free, petroleum feedstock.

A readily available domestic source of vanadium is the fly ash produced by the Suncor and Syncrude plants involved in petroleum recovery from the Athabasca Oil Sands. The fly ash produced by Suncor Inc. at Fort McMurray, Alberta, contains 2 to 3% vanadium — a concentration typical of vanadium ores. Potentially, 2000 tonnes of vanadium

pentoxide per year could be recovered from the throughput of the two oil sands plants. This production would be equivalent to 12% of the vanadium production in western world countries in 1980 (1).

Interest has also been expressed in the extraction of other metals from oil sands fly ash; in particular, nickel (5, 6) and molybdenum (7) which occur in Suncor fly ash in concentrations of 1% and 0.2%, respectively. The use of fly ash derived from hydrocarbon fuels as an alternative source of various metals has been under investigation in many laboratories (8). The extraction of metals from fly ash is also of interest because of the possibility of Canadian legislation similar to the United States Resource Conservation and Recovery Act (1976) that requires that certain leachable elements be extracted prior to disposal (8). Water leaching of metals from fly ash placed into landfill can cause contamination of the ground and surface water systems. This problem is particularly serious with coal fly ash which contains heavy metals such as arsenic and lead.

This thesis centers on the extraction of vanadium from Athabasca oil sands derived fly ash. The first part describes the extraction of vanadium from Suncor fly ash roasted with sodium chloride and leached with hot water. The effects of various factors on the sodium chloride roast process were determined and the roasting conditions optimized. Precipitation of vanadium from the leachate as

red cake or ammonium metavanadate was also studied. The second part of this study concerns the extraction of vanadium and nickel from the ash of laboratory-generated low-sulfur-emission oil sands coke. The leaching process and various methods of purification and precipitation of vanadium from solution were investigated.

II. LITERATURE SURVEY

A. Occurrence, World Production, and Use of Vanadium

The average crustal abundance of vanadium is 0.02%, which makes it the eighth most abundant element. More than sixty vanadium bearing ores are known; however, few contain concentrations in excess of 2 to 3% vanadium (9, 10, 11, 12).

Forty-eight percent of the world vanadium reserves occur in South Africa, and 46% in the USSR (13). The main vanadium-producing nations and their relative productions in 1980 were: South Africa (35.8%); USSR (28.2%); United States (12.3%); China (12.7%); and Finland (8.5%) (14). The main source of vanadium in South Africa, the USSR, China, and Finland is vanadium-bearing magnetite or slags derived from them. Uranium-bearing ores, fly ash, vanadiferous shales, vanadiferous clays, and phosphate ores are the United States' sources. Vanadium is usually produced as a by-product of iron, uranium, or petroleum production operations; however, the vanadiferous clays of Arkansas are an example of a case in which vanadium has been recovered from an ore as the sole product (15).

The major consumers of vanadium in 1980 were the USSR (37.1%); Western Europe (25.8%); the United States (19.5%); and Japan (8.7%) (1). Canadian consumption in 1980 was less than 2% of the world consumption (1). The concentration of vanadium reserves and production capacity

in South Africa and the USSR has caused alarm among western nations (16, 17, 18). Decreasing uranium production in the United States and the accompanying decrease in vanadium production has added to the concern. The potential insecurity of future supplies of vanadium has stimulated interest in the development of domestic supplies in western nations (17).

The world steel industry consumes over 90% of the total vanadium production (15). High-speed tool steels contain 1 to 5% vanadium, much of which is present as vanadium carbide which gives the required hardness and strength. The steadily increasing consumption of vanadium is attributed to the increasing use of high-strength, low-alloy (HSLA) steels containing 0.03 to 0.08% vanadium. In these steels addition of vanadium increases strength and toughness through grain refinement and precipitation hardening (1, 15). Because of their high strength to weight ratio, HSLA steels have found increasing use in high pressure pipelines, in the automotive industry, and as structural steel (19). Vanadium is also used in titanium alloys and as a substitute for molybdenum in steels because of the high cost and unreliability of molybdenum supplies (20). If vanadium was substituted for 10% of the total molybdenum used in steels (mole/mole basis), the vanadium requirement would equal nearly 20% of the world vanadium production capacity (21).

Vanadium catalysts used in the petrochemical industry account for approximately 2% of the total vanadium usage.

These catalysts are used in the conversion of sulfur dioxide to sulfur trioxide; reduction of olefins; and various oxidations such as the conversion of benzene to maleic anhydride, cyclohexane to adipic acid, and naphthalene to phthalic anhydride (15, 20).

Most of the world vanadium is produced in the form of vanadium pentoxide (V_2O_5). Ferrovanadium (35-95% vanadium), produced by simultaneous reduction of iron and vanadium oxides by carbon or silicon (22), and other alloys are of lesser importance. Vanadium metal is produced by metallothermic reduction with aluminum metal (22). Ultrapure vanadium metal is obtained by the de Boer-van Arkel process in which purified vanadium tetraiodide vapor is thermally decomposed on hot wire in a vacuum (12). Vanadium metal finds limited commercial use, however, because of its high reactivity with oxygen, hydrogen, nitrogen, and carbon at high temperatures and the accompanying loss of ductility (9, 11).

B. Extractive Metallurgy of Vanadium: Industrial Practice

The most common industrial method of recovering vanadium is an alkali-salt roast/hot-water leach process. The alkali salt is sodium chloride, sodium carbonate, or sodium sulfate. The original patent for the sodium chloride roast/hot-water leach process was obtained by Bleecker (23) in 1912. Many variations have subsequently appeared in the patent literature (24). In the sodium chloride roast

process, the feed is mixed with the alkali salt and roasted in air in multiple hearth roasters or rotary kilns for 1 to 5 hr at 800 to 900°C. During this time the alkali reacts with the vanadium to form water-soluble sodium vanadate. Leaching with hot water results in typical extractions of 65 to 85% (25).

Mineral beneficiation prior to roasting is not normally a part of the recovery process because of the low concentration of vanadium in the vanadium bearing minerals. However, a "concentrate" is often produced as a by-product of iron, uranium, or petroleum production.

Titaniferous Magnetites

At the Highveld Steel and Vanadium Co. plant in South Africa, titaniferous magnetite is prereduced in coal-fired rotary kilns. Ninety percent of the vanadium in the ore segregates to the pig iron that is subsequently formed. When the pig iron is blown with oxygen to remove carbon, the vanadium is oxidized and a vanadium rich slag containing 15 to 25% vanadium pentoxide is formed (26). The slag is then salt roasted and water leached to extract vanadium.

At Otonmaki, Finland, vanadium is extracted directly from titaniferous magetites (26). A magnetite concentrate obtained by magnetic separation is mixed with sodium carbonate, pelletized, and roasted. The iron-rich pellets remaining after hot-water leaching are sold as an iron concentrate.

Clays and Shales

Vanadiferous clays in Hot Springs, Arkansas have been used as a commercial source of vanadium by Union Carbide. The clays are mixed with high grade slag to produce a feed containing 1.7% V_2O_5. The feed is mixed with 10% sodium chloride and roasted in a rotary kiln for 2 hr at 850°C.

Vanadiferous shales containing 1% V_2O_5 are found in several sections of the United States. Eighty percent of the vanadium can be extracted from the shales in Carlin, Nevada by roasting with 5% sodium chloride at 900°C for 3 hr, and leaching with dilute sulfuric acid. The shales contain appreciable calcia and magnesia (15% CaO + MgO) which react during roasting to form calcium and magnesium vanadates. These vanadates dissolve in acid but not in water, hence necessitating the use of acid leachates (25).

Uranium Ores

The sodium chloride roast process has been the predominant process by which uranium and vanadium are extracted from Colorado Plateau ores. The ore is roasted with sodium chloride at 800 to 850°C for 1 to 2 hr. The roast is leached first with hot water which extracts about 80% of the vanadium, and then with sulfuric acid which extracts most of the uranium and the remaining vanadium. In other operations, the roast is leached directly with sulfuric acid, and the uranium and vanadium are simultaneously extracted and separated by solvent extraction

or selective precipitation (26).

Fly Ash and Bottom Ash

Fly ash derived from petroleum has become an important commercial source of vanadium in recent years. Heavy crudes, such as those produced by Venezuela, contain 300 to 1200 ppm vanadium (27). The Long Island Lighting Company (LILCO) in the United States recovers vanadium from bottom ash formed during the combustion of Venezuelan crude at its electric power generating plant. Although power generation is the company's main interest, its vanadium production was equivalent to 5.5% of the total vanadium consumption in the United States in 1973 (28).

In 1967, Canadian Petrofina opened a vanadium extraction plant, near its Montreal refinery, which produced 200 tonnes of vanadium pentoxide per year. The feed for the plant was fly ash obtained through combustion of hydrocarbon residues produced from refining Venezuelan crude. The fly ash, containing 13 to 15% V_2O_5 equivalent (30% on a carbon-free basis), was leached with 2M sulfuric acid at 50°C. The vanadium in the filtered leachate was oxidized from the tetravalent to the pentavalent oxidation state with sodium perchlorate, and precipitated as vanadium pentoxide by increasing the pH from 0.3 to 1.7. The vanadium pentoxide was dried, fused, and flaked, resulting in a final product which contained 99% V_2O_5 (4, 29, 30, 31).

C. Athabasca Oil Sands Fly Ash as a Source of Vanadium

Athabasca bitumen contains 200 ppm vanadium, 80 ppm nickel, 4.6% sulfur, and 0.5 to 1.0% mineral matter. In industrial petroleum recovery operations, the bitumen is separated from the sand by the Clark hot-water process and is upgraded by thermal cracking and hydrotreating to synthetic crude (32). The Suncor and Syncrude plants near Fort McMurray, Alberta have a combined production of nearly 200,000 barrels per day of synthetic crude.

The vanadium in the bitumen occurs primarily as metal-porphyrin complexes (29, 33, 34, 35). The high thermal stability and low vapor pressure of these complex molecules results in their retention in the coke produced during thermal cracking. Combustion of the coke in utility boilers further concentrates the vanadium in the ash. The behavior of nickel is similar to that of vanadium. The Suncor fly ash contains 1 to 2% vanadium, 0.5 to 1.0% nickel, and 40 to 60% unburned carbon (5).

Examination of Suncor fly ash by scanning electron microscopy (SEM) showed that it consisted of aluminosilicate spheres and irregularly-shaped porous char particles (5, 36, 37). Microcrystals enriched in vanadium, nickel, iron, and titanium were also observed (5). This morphology is consistent with that observed in fly ash collected from coal-fired power plants (38, 39). Studies on the formation of coal fly ash show that the aluminosilicate spheres originate from the inorganic inclusions in the coal. These

inclusions are normally a mixture of silica, aluminosilicates (e.g., clay minerals), iron compounds, and calcium compounds. As the parent coal or coke particles pass through the combustor (900 to 1500°C, 2 to 4 sec), the inclusions melt forming smooth-surfaced spheres that retain their shape upon cooling. The crystal structures are thought to arise through condensation and crystallization of volatiles formed from the inorganics or from the eventual crystallization of amorphously formed solids (40). The rough porous particles are char particles from the incomplete combustion of the coal particles.

Vanadium, nickel, and the trace metals in Suncor fly ash are associated with the aluminosilicate spheres, as shown by analysis of a mineral concentrate which was separated from the unburned carbon by froth flotation (41). The mineral concentrate contained less than 0.3% of the total amount of carbon in the starting sample, but contained 85.9% of the vanadium, 89.2% of the nickel, and 83.0% of the iron.

Previous Studies on the Extraction of Vanadium from Suncor Fly Ash

The first attempts to extract vanadium from Suncor fly ash showed that vanadium could not be extracted by a simple acid leach such as that used by Petrofina (36). The difference was attributed to the high aluminosilicate content of Suncor fly ash. At the high temperatures of combustion, the aluminosilicates contained in the coke or

coal particles form a glassy phase in which metals such as vanadium become physically or chemically entrapped (42). Laboratory tests confirmed that the combustion temperature affects the extent to which vanadium and nickel can be leached from the ash (6, 43). Ninety-nine percent of the vanadium and 80% of the nickel were extracted by acid leaching the ash from Suncor coke burned at 500°C, but only 55% of the vanadium and 4% of the nickel were extracted when the coke was burned at 900°C (6).

The recovery of vanadium and nickel from Suncor fly ash by pyrometallurgical techniques was reported in 1975 by Stemerowicz, et. al. (41). Reduction of nickel, iron, and vanadium to form a ferro-nickel-vanadium alloy followed by selective oxidation to form a vanadium rich slag and a ferro-nickel alloy appeared to be the most feasible of the methods investigated. Matte smelting to form nickel matte followed by metallothermic reduction to form ferro-vanadium, or two-stage selective reduction to produce ferro-vanadium and ferro-nickel gave unsatisfactory separation of vanadium, nickel and iron. Further, the loss of metals in the slag was high (10 to 20%) because of the high slag to metal ratio.

Extraction of vanadium by leaching or by a combined roast/leach procedure was investigated by Griffin and Etsell (5, 44, 45). The various methods investigated were:

1. Direct leaching with water, acid, or base;
2. Roasting in an oxidizing, inert, or reducing atmosphere followed by leaching with water, acid, or base;

3. Roasting with various inorganic salts (NaCl, Na_2CO_3, KCl, $CaCl_2$, $CaCO_3$, Na_2SO_4) followed by leaching with water or acid;
4. Roasting in an atmosphere of chlorine gas to convert vanadium to gaseous vanadyl chloride ($VOCl_3$) or vanadium tetrachloride (VCl_4).

The most promising results were obtained by roasting the fly ash with sodium chloride and leaching the roast with hot water. Subsequent optimization studies showed that 90% of the vanadium was extracted with hot water when the fly ash was roasted with 14% sodium chloride at 905°C for 6 hr in air. The fly ash was roasted in a porcelain boat placed in an open horizontal tube furnace. Nickel was not extracted by the sodium chloride roast process. The same study by Griffin and Etsell showed that 94% of the nickel could be recovered in an alternate process in which the ash was roasted with 15% elemental sulfur followed by leaching in hot, 10% sulfuric acid.

Application of the sodium chloride roast process was also studied by Gomez-Bueno, Spink, and Rempel (46, 47). In their study the fly ash was decarbonized by roasting in air at 500°C and subsequently roasted with sodium chloride in water-saturated nitrogen with a rotary screw roaster. Under optimum roasting conditions (5 to 10% sodium chloride, 875 to 920 °C, 0.39 atm water vapor in nitrogen), 85% of the vanadium was extracted by leaching the roast with a 2M sodium hydroxide solution. Only trace amounts of vanadium

were extracted by leaching with hot water. If experiments were conducted in which the fly ash/sodium chloride mixture was roasted in air and the roast leached in hot water, they were not reported.

Extraction of Vanadium from the Ash of Low-Sulfur-Emission Coke

The recovery of vanadium (and other metals) from oil sands fly ash is dependent upon the production of fly ash through combustion of the coke. The coke produced by Suncor contains 6% sulfur and that produced by Syncrude contains 6 to 8% sulfur. Only part of the coke produced is being burned because of government regulations restricting the amount of sulfur dioxide that can be released to the environment. Within the guidelines, Suncor is able to burn over 80% of its coke production or 2450 tonnes/day. In contrast, Syncrude is able to burn only 20% of its coke production (600 tonnes/day) because of high sulfur dioxide emissions from elsewhere in its operations.

In response to this problem, a method was developed by George, Schneider, and Kessick (48) for the production of coke with a low sulfur emission. Bench-scale experiments showed that mixing 4.8% calcium hydroxide with bitumen prior to coking produced a coke that released only 1% sulfur as sulfur dioxide during combustion at industrial combustion temperatures (48). The sulfur dioxide emission was reduced from the usual 6 to 8% because the sulfur in the coke reacted with calcium hydroxide to form calcium sulfate which

remained in the ash. Calcium hydroxide also had beneficial effects on the extraction of vanadium and nickel from the ash of the coke (6). Ninety-eight percent of the vanadium and 82% of the nickel were extracted by leaching with 2M hydrochloric acid at 95°C. The leaching was optimized with respect to the leachate used, leaching temperature, and leaching time. Although it was necessary to add 4.8% calcium hydroxide to the bitumen to reduce the sulfur emission to a satisfactory level, as little as 0.5% calcium hydroxide was adequate for extraction of 90% of the vanadium from the ash by acid leaching. The vanadium in the ash is likely present as calcium pyrovanadate ($Ca_2V_2O_7$) or calcium orthovanadate ($Ca_3(VO_4)_2$). These compounds are soluble in acid solution but insoluble in water. Calcium metavanadate ($Ca(VO_3)_2$) would not be present as it melts with decomposition at 775°C (49).

The chemical reactions by which the calcium reagent liberates the metals are probably similar to those in the Calsinter Process (50, 51). In this bench-scale process, fly ash from coal fired plants is roasted with calcium carbonate at 1000 to 1200°C to convert the aluminosilicates to anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) and gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$). This breaks the glassy aluminosilicate matrix, freeing the entrapped metals which can be subsequently leached with dilute acid.

D. The Chemistry of the Sodium Chloride Roast Process

Burwell suggested that vanadium processing has developed more as an art than as a science, with the conditions for optimum extraction determined more often by trial and error than by knowledge of the process itself (52). A survey of the recent literature showed that the chemistry of the salt-roast process is still not well understood. Any study of vanadium chemistry is difficult because vanadium can exist in a number of oxidation states, and can combine chemically with many other elements to form closely related compounds. Many of these compounds are nonstoichiometric and contain vanadium in more than one valence state.

Chemical Reactions

Sodium chloride reacts with vanadium pentoxide and water vapor to form sodium metavanadate, Eq.[1] (24).

$$2NaCl + V_2O_5 + H_2O(g) \rightarrow 2NaVO_3 + 2HCl \qquad [1]$$

At 850°C the free energy of reaction is 0.30 kcal/mole (47). The solubility of sodium metavanadate at 25°C is 212 g/l of water (53).

In the absence of water vapor, NaCl reacts with V_2O_5 and oxygen to form sodium metavanadate and chlorine gas, Eq.[2].

$$2NaCl + V_2O_5 + 1/2\ O_2 \rightarrow 2NaVO_3 + Cl_2 \qquad [2]$$

Evolution of hydrogen chloride gas is observed in industrial processes (26), presumably because moisture is normally

present in both the feed and the air.

Sodium pyrovanadate ($Na_4V_2O_7$), another water soluble compound, is reported to form from sodium metavanadate and water vapor upon prolonged roasting (24), Eq.[3].

$$2NaCl + H_2O(g) + 2NaVO_3 \rightarrow Na_4V_2O_7 + 2HCl(g) \quad [3]$$

Sodium carbonate and sodium sulfate also react with vanadium pentoxide to form sodium metavanadate, Eq.[4] and Eq.[5] (24).

$$Na_2SO_4 + V_2O_5 \rightarrow 2NaVO_3 + SO_3 \quad [4]$$

$$Na_2CO_3 + V_2O_5 \rightarrow 2NaVO_3 + CO_2 \quad [5]$$

These compounds are normally used in the salt roasting of low silica titaniferous magnetite. Titaniferous magnetite is roasted with the salt in excess air at 1000 to 1300°C. This oxidizes the iron in the spinel structure (i.e., $(Fe,V)_3O_4$) to hematite (Fe_2O_3), thus breaking the spinel structure and liberating the vanadium for reaction with the alklali salt. Sodium carbonate and sodium sulfate are used in preference to sodium chloride because the molten sodium chloride serves as a barrier to the oxygen required for the oxidation of the spinel.

Side Reactions

The successful use of the salt-roast process involves minimizing the various deleterious side reactions.

1. Formation of Water Insoluble Vanadium Compounds

An inadequate amount of salt, moisture, or oxygen can result in the formation of water insoluble "bronzes"

(24). The "bronzes" are alkali polyvanadates which contain vanadium in both the pentavalent and tetravalent oxidation state. An example is NaV_6O_{15} which contains one tetravalent and five pentavalent vanadium ions (24). Vanadium "bronzes" can also form when the roasted solid is cooled slowly rather than quenched (54). The phase diagram for the Na_2O-V_2O_5 binary system in 0.20 or 1.0 atm oxygen shows that melts containing 50 mole % or more of vanadium pentoxide lose oxygen as they are cooled. Solidification occurs at 650 to 550°C with the formation of $5Na_2O \cdot xV_2O_4 \cdot (12-x)V_2O_5$ and $Na_2O \cdot xV_2O_4 \cdot (6-x)V_2O_5$ which more correctly belong in the Na_2O-V_2O_4-V_2O_5 system (55).

Basic calcium compounds such as calcium carbonate react with vanadium pentoxide at temperatures from 600 to 765°C to form various calcium vanadates (24, 56). Calcium sulfate is reported as less reactive than calcium carbonate (52). In the CaO-V_2O_5 binary system, three compounds are well defined (49): calcium metavanadate ($Ca(VO_3)_2$), calcium pyrovanadate ($Ca_2V_2O_7$), and calcium orthovanadate ($Ca_3(VO_4)_2$). The solubility of calcium metavanadate in water is 2 to 4 g/l at 25°C (57, 58) and the solubility of calcium pyrovanadate and calcium orthovanadate is less than 2 g/l (24, 59). Calcium "bronzes" such as $CaV_{12}O_{30}$ can also form under low oxygen pressure at 400 to 600°C (24, 60, 61). However, in air they oxidize to form calcium vanadate containing only pentavalent vanadium.

Other water-insoluble vanadium compounds can also form. For example, iron and aluminum compounds can react to form insoluble iron vanadate ($Fe(VO_3)_3$) and aluminum vanadate ($Al(VO_3)_3$) (62).

2. Consumption of Salt by Silicates and Aluminosilicates

The alkali reagent can react with the silica or aluminosilicate in the feed with the consequence that there is insufficient alkali to react with the vanadium. The sodium salts react with silica to form sodium silicate (Na_2SiO_3). Sodium chloride reacts by the water glass reaction, Eq.[6],

$$NaCl + SiO_2 + H_2O \rightarrow HCl + NaSiO_3 \qquad [6]$$

which is thermodynamically favorable, although slow, at 800 to 1000°C. Sodium chloride tends to be less reactive than sodium carbonate or sodium sulfate and is normally used when the feed contains appreciable silica (52). Sodium chloride can also react with kaolinite ($Al_2Si_2O_5(OH)_4$) to form sodalite ($Na_8(AlSiO_4)_6Cl_2$) (24, 63).

3. Occlusion of Vanadium in Silicate Glass

In the sodium chloride roast process, the optimum roasting temperature is normally between 800 and 900°C. The decrease in vanadium extraction above this temperature is attributed to the physical or chemical incorporation of vanadium in silicate and aluminosilicate glasses that are present in the feed or formed during roasting. Although this entrappment is

widely discussed in the literature, little is known of its chemistry.

Several studies suggest that the vanadium is chemically incorporated into the glass. The presence of trivalent, tetravalent and pentavalent vanadium ions in glass has been reported, with pentavalent vanadium being the only valence state at 1085°C when oxygen is present (64). A detailed laboratory study of vanadium entrappment in glassy phases formed during the salt roasting of vanadiferous magnetites also suggested chemical incorporation of vanadium (42). Examination of the feed before and after roasting by scanning electron microscopy showed that a smooth homogeneous glassy phase formed as the roasting temperature was increased through the optimum. Chemical analysis by energy dispersive X-ray analysis showed that the vanadium was transferred from the spinel to the glassy phase. The glassy phase appeared homogeneous, suggesting the vanadium was atomically dispersed or chemically bonded.

Equilibrium phase diagrams suggest that alumina must be present if chemical incorporation is to occur. The phase diagram for the Al_2O_3-SiO_2-V_2O_5 system shows an unidentified ternary compound in which the alumina to silica ratio is 1:2 and the vanadium pentoxide concentration varies from zero to 98% (65). In the SiO_2-V_2O_5 binary system, however, quartz and vanadium pentoxide are the only solid phases; an intermediate

phase consisting of silica combined with vanadium pentoxide is not observed (66).

4. Carbonaceous Material

The presence of carbonaceous material has been reported as deleterious to the salt roasting of vanadiferous shales (25, 52). Weathered shales at the surface of the deposit, typically containing 1% carbon, can be salt roasted directly. In comparison, subsurface shales containing 10% carbon must be preroasted (2 hr, 700°C) to remove the carbon prior to salt roasting to obtain similar extraction (24, 25). The investigators suggest that during roasting the carbon interferes in the reaction between vanadium and the salt by reducing the vanadium.

Kinetics and Mechanisms of the Salt Roast Process

Little is known about the kinetics or mechanisms of the alkali salt roast process. In one of few kinetics studies, Dresher (67) observed that the reaction rate of sodium chloride with vanadium pentoxide was logarithmic in dry air, suggesting it was controlled by diffusion of oxygen through a surface layer of reaction products. In wet air the reaction was first order with respect to water vapor.

The so called "two-step" mechanism of the sodium chloride roast process has been widely discussed in the literature but experimental evidence is lacking (68). In this mechanism sodium oxide is formed through the oxidation

of sodium chloride or the dissociation of sodium sulfate or sodium carbonate, and the sodium oxide subsequently reacts with vanadium pentoxide to form sodium vanadate. The oxidation of sodium chloride is somewhat doubtful because the free energy change for the reaction at 927°C is 85 kcal/mole (69). In the case of sodium carbonate and sodium sulfate, appreciable reactivity with vanadium pentoxide is observed at 500°C, a temperature at which the dissociation pressures are negligible. Further, the relative reactivities of various alkali salts with vanadium pentoxide do not correspond to their relative thermal stabilities.

A more convincing mechanism proposed by Fotiev (68, 70, 71) is that the reaction between the alkali salt and vanadium pentoxide is controlled by the diffusion of alkali cations into the vanadium pentoxide crystal structure. The rate of reaction and the crystal lattice energy of various commonly used alkali salts were inversely related and the maximum rate of reaction occured at increasingly higher temperatures for those compounds of increasingly higher lattice energy. Cations on the surface of the alkali crystals diffuse into the vanadium pentoxide matrix leaving behind vacancies through which other alkali metal cations may diffuse. The anions react under energetically more favorable conditions to form hydrogen chloride, chlorine gas, carbon dioxide, or sulfur dioxide, depending upon the alkali salt used.

This mechanism is consistent with some of the reaction intermediates that have been reported. For example, in a reaction mixture composed of sodium chloride and vanadium pentoxide, compounds of progressively higher sodium content formed until the final product sodium metavanadate was reached, Eq.[7] (72).[1]

$$\{NaCl + V_2O_5\} \rightarrow NaV_6O_{15} \rightarrow Na_8V_{24}O_{63} \rightarrow NaVO_3 \qquad [7]$$

At 600°C, NaV_6O_{15} formed from the starting mixture within one minute (73, 74). As further evidence for this mechanism, Fotiev found that vanadium pentoxide and the first reaction product (NaV_6O_{15}) share common structural elements (68). The vanadium pentoxide crystal contains chains of trigonal bipyramids which are interspersed with vacant channels. In NaV_6O_{15} the trigonal bipyramid structure persists and sites within the channels are occupied by sodium ions.

The Fotiev mechanism explains the high reactivity observed between vanadium pentoxide and the alkali salts in a totally solid state reaction system. However, because of the high temperatures used in the industrial salt roast process, the role of liquid phases must also be considered. The phase diagrams of the binary systems V_2O_5-$NaVO_3$, V_2O_5-Na_2O, V_2O_5-Na_2SO_4, and V_2O_5-Na_2CO_3 all contain one or more eutectics in the 550 to 650°C range (75). Furthermore, in these systems a single phase liquid is stable over almost

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[1]This reaction sequence requires the presence of air or oxygen to oxidize vanadium from the +4.83 oxidation state in NaV_6O_{15} through +4.92 in $Na_8V_{24}O_{63}$ to +5.00 in $NaVO_3$. The chloride in sodium chloride is evolved as chlorine or hydrogen chloride, depending upon the presence or absence of water.

the entire range of composition at temperatures above 700°C. The formation of liquid phases could explain the high reactivity observed between the commonly used alkali salts and vanadium pentoxide at temperatures at which the pure substances are solids.

E. The Chemistry of Vanadium in Aqueous Solution

The chemistry of pentavalent vanadium in aqueous solution is characterized by a large number of species which interconvert in numerous hydrolysis and condensation reactions for which the thermodynamics and kinetics are poorly known. The current knowledge of pentavalent vanadium is summarized in Figure 1. This "predominance-area diagram" shows the predominant ionic species as a function of pH and total vanadium concentration in solution (76). In strongly alkaline solutions, the predominant vanadium species is the orthovanadate ion (VO_4^{-3}). As the pH is decreased this species is hydrolyzed to the monomeric pyrovanadate ion (HVO_4^{-2}), Eq.[8], with a pK ≃ 13.

$$VO_4^{-3} + H_2O \leftrightarrow HVO_4^{-2} + OH^- \qquad [8]$$

Monomeric pyrovanadate condenses and dehydrates to form dimeric pyrovanadate ($V_2O_7^{-4}$) when the vanadium concentration in solution exceeds 5 g/l V_2O_5, Eq.[9].

$$2HVO_4^{-2} \leftrightarrow V_2O_7^{-4} + H_2O \qquad [9]$$

As the pH is further decreased, monomeric pyrovanadate is protonated to metavanadate ($H_2VO_4^-$), Eq.[10], with a pK≃ 8.

$$HVO_4^{-2} + H_2O \leftrightarrow H_2VO_4^- + OH^- \qquad [10]$$

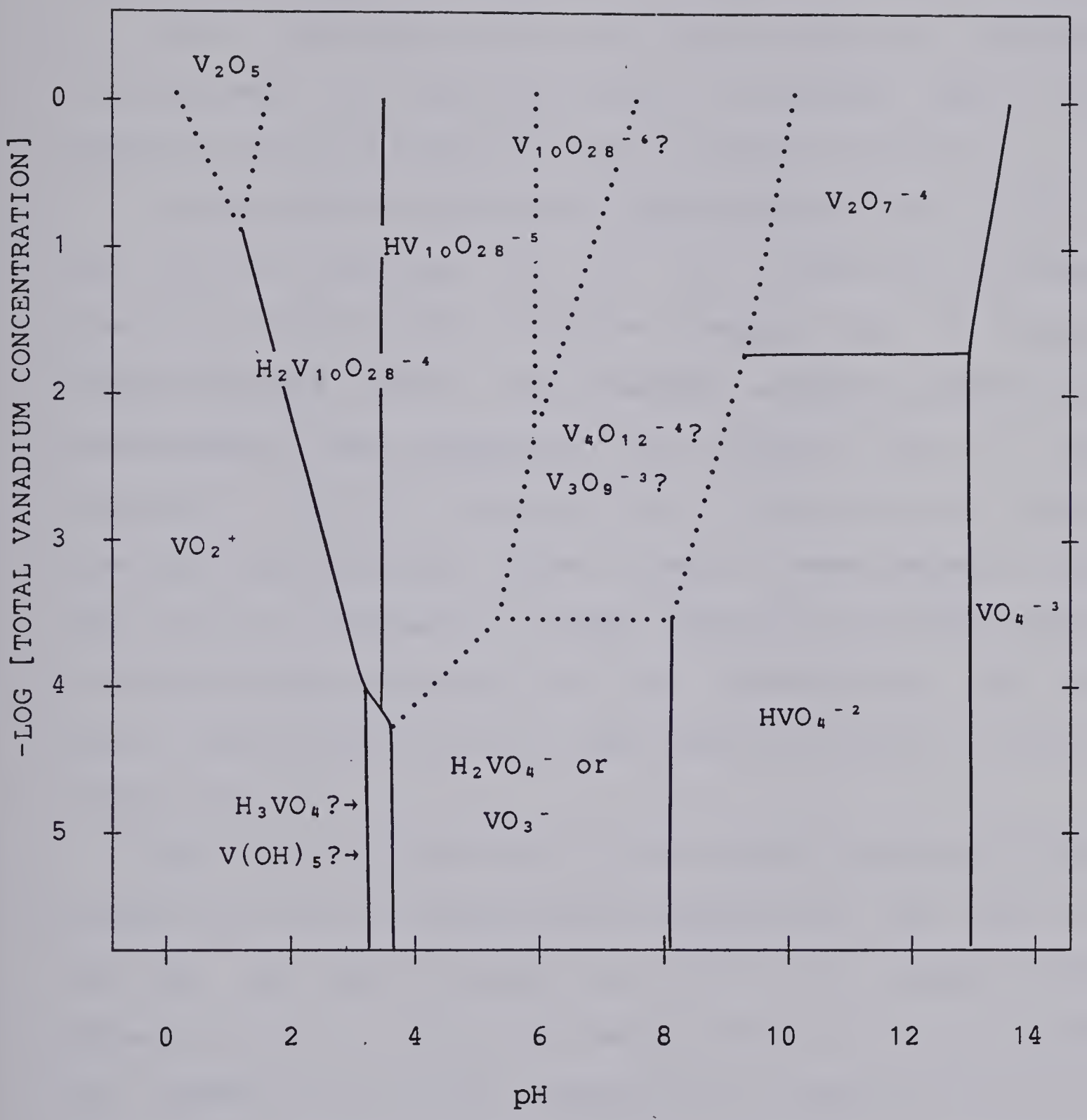

Figure 1. Predominance Diagram for Pentavalent Vanadium in Aqueous Solution (76).

The $H_2VO_4^-$ species is commonly written as VO_3^-, the nonhydrated form of metavanadate. At a pH of about 3.5, vanadic acid forms. Its chemical formula is written either as $V(OH)_5$ (hydrated with one water molecule) or H_3VO_4 (nonhydrated). In strongly acidic solutions (pH < 3), vanadium exists as the pale yellow vanadyl ion (VO_2^+).

Vanadic acid and monomeric metavanadate occur only in very dilute solutions ($\leq 10^{-4}$ g/l vanadium). At higher vanadium concentrations, various complex and ill-defined polymerizations occur. Experimental evidence suggests the metavanadate ions polymerize to trimeric ($V_3O_9^{-3}$) and tetrameric ($V_4O_{12}^{-4}$) species. At a lower pH and a higher vanadium concentration, the orange decavanadate ions ($HV_{10}O_{28}^{-5}$ or $H_2V_{10}O_{28}^{-4}$) form. There is good experimental evidence for the existence of the decavanadate ions but their interconversion with other vanadium species is poorly understood (12).

The solution chemistry of tetravalent vanadium is much simpler than that of pentavalent vanadium (77, 78, 79). At low pH, the blue vanadyl ion (VO^{+2}) is stable in the presence of air. As the pH is raised above 2, the vanadyl ion becomes increasingly susceptible to oxidation by air to pentavalent vanadium species. If the solution of tetravalent vanadium is kept under hydrogen during neutralization, oxidation does not occur and vanadyl hydroxide ($VO(OH)_2$) begins to precipitate at a pH of 4.3.

The electrochemical series for vanadium is shown in Eq.[11], [12], [13], and [14] (53, 80).

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{+2} + H_2O \quad [11]$$
$$E^\circ = 1.00 \text{ volts}$$

$$VO^{+2} + 2H^+ + e^- \rightarrow V^{+3} + H_2O \quad [12]$$
$$E^\circ = 0.337 \text{ volts}$$

$$V^{+3} + e^- \rightarrow V^{+2} \quad [13]$$
$$E^\circ = -0.255 \text{ volts}$$

$$V^{+2} + 2e^- \rightarrow V \quad [14]$$
$$E^\circ = -1.2 \text{ volts}$$

The series shows that vanadium is successively reduced from the pale yellow vanadyl ion (VO_2^+), through the blue vanadyl ion (VO^{+2}) and the green vanadic ion (V^{+3}), to the violet vanadous ion (V^{+2}). The final reduction to vanadium metal is accompanied by reduction of water to hydrogen which makes electrowinning of vanadium from aqueous solution impractical.

F. The Conversion of Vanadium in the Leachate to Vanadium Pentoxide

The vanadium in the leachate can be converted to vanadium pentoxide by several different methods depending upon the concentration of vanadium in the leachate, the concentration of impurities in the leachate, and the required purity of the final product.

Precipitation of Red Cake

The most direct way to recover vanadium pentoxide from aqueous solution is by precipitation of red cake. Red cake

has a nominal composition of $Na_2H_2V_6O_{17}$ (sodium hexavanadate), although the actual composition can vary from 85 to 95% V_2O_5 depending upon the conditions during precipitation and the leachate composition (81).

To precipitate red cake, the pH of the hot leachate is adjusted to 2-3 by addition of hydrochloric or sulfuric acid. Precipitation of red shot-like particles begins immediately and precipitation is complete in less than an hour. The solid is readily filtered from the aqueous solution which contains 0.1 to 1.0 g/l V_2O_5 (81, 82). Some manufacturers dry and fuse the red cake to form a black vanadium oxide (black cake) which is sold as the final commercial product. Red cake may also be purified by procedures described below to form high purity vanadium pentoxide.

Precipitation of Ammonium Hexavanadate

Ammonium hexavanadate (orange cake) can be precipitated by adding ammonium chloride to the leachate and immediately acidifying (26). The orange solid is filtered, fused, and flaked to form a product containing 98% V_2O_5 and 0.4% Na_2O. Several investigators (81, 82) report that a low alkali product could not be recovered by this method and that the ammonium vanadate was heavily contaminated with sodium and potassium.

Production of High Purity Vanadium Pentoxide

More manufacturers are producing high purity vanadium pentoxide (≥ 99% V_2O_5). The processes normally used involve the precipitation of ammonium metavanadate which is then thermally decomposed to high purity vanadium pentoxide.

1. Upgrading Red Cake

   The main impurity in red cake is sodium with potassium, silica, iron and other elements normally present at significantly lower concentrations. Red cake can be purified by dissolving it in hot sodium carbonate solution, and precipitating ammonium metavanadate by addition of ammonium chloride or ammonium sulfate (31, 82). Laboratory studies showed that the amount of ammonium chloride required for the efficient precipitation of ammonium metavanadate from the sodium carbonate solution reached a minimum (weight ratio $NH_4Cl:V_2O_5$ = 1) when both the vanadium concentration in solution and the weight ratio of vanadium pentoxide to sodium carbonate were high (100 g/l V_2O_5, $V_2O_5:Na_2CO_3$ = 1.5) (31).

   Red cake has also been dissolved in a hot solution of ammonium hydroxide and ammonium chloride to yield a solution containing 30 g/l V_2O_5 equivalent at a pH of 7.2. When the temperature was reduced to ambient, ammonium metavanadate precipitated (81).

2. Solvent Extraction

Solvent extraction is used for the production of highly pure vanadium pentoxide (>99% V_2O_5). Commercially available extractants have a high selectivity which allows vanadium to be readily extracted from aqueous feeds containing high concentrations of impurities. Further, solvent extraction is the only method available by which vanadium can be efficiently extracted from aqueous feeds containing low concentrations of vanadium (25). Ninety-eight to 99% of the vanadium can be extracted from a leachate containing 1 to 2 g/l V_2O_5 (25, 83, 84). The methodology for solvent extraction of vanadium underwent intensive development in the United States in the early 1960s due to the increase in uranium production and the resultant recovery of vanadium as a by-product. In 1966 eleven vanadium solvent extraction plants were operating in the United States (83).

Tertiary amines (e.g., Alamine 336) and quaternary amines (e.g., Aliquat 336) dissolved in kerosene are commonly used for the extraction of pentavalent vanadium (83, 85). In these systems, the polyanionic vanadium ions in the aqueous phase form kerosene-soluble ion-pairs with the positively charged amine (84). Tertiary amines are useful for the extraction of vanadium only when the aqueous solution is acidic as they must be protonated in order to be active as extractants. Quaternary amines which carry a permanent positive charge can be used over a pH range of 2 to 9

(85, 86). When the concentration of vanadium in the aqueous phase drops below 1 to 2 g/l, the extraction efficiency drops because of the dissociation of the polyanionic vanadium species.

After the extraction of the aqueous feed, the loaded organic is contacted with the stripping solution, typically 2M sodium carbonate if the extractant is Alamine 336 or 1.5M ammonium chloride/1.5M ammonia if the extractant is Aliquat 336. By minimizing the organic to aqueous phase ratio during extraction and maximizing it during stripping, the vanadium concentration in the stripper can be raised substantially over that in the aqueous feed. Ammonium metavanadate can be precipitated from the carbonate stripper by addition of ammonium chloride. In the case of the ammonium chloride/ammonia stripper, the vanadium is simultaneously stripped and precipitated as ammonium metavanadate.

3. Precipitation and Thermal Decomposition of Ammonium Metavanadate.

Ammonium chloride is added to alkaline solutions of pentavalent vanadium to precipitate high-purity ammonium metavanadate (Eq.[15]) (82).

$$NaVO_3 + NH_4Cl \rightarrow NH_4VO_3 + NaCl \qquad [15]$$

At 25°C, the solubility of ammonium metavanadate is 0.031 g/l in a 0.10M solution of ammonium chloride compared to 7.70 g/l in pure water(87).

A practical problem in ammonium metavanadate precipitation is the excessive amounts of ammonium salts required to achieve high levels of precipitation from alkaline leachates or from leachates containing vanadium concentrations of less than 30 g/l V_2O_5 (31). This occurs because the ammonium metavanadate solubility is greatly affected by the concentration of other sodium and vanadium compounds in solution (87). For example, sodium chloride which is originally present in the feed or formed through the precipitation of ammonium metavanadate (Eq.[15]) reduces the extent to which ammonium metavanadate precipitates. If the leachate is excessively alkaline, ammonium chloride is consumed by a series of hydrolysis reactions (Eq.[16] and [17]) prior to the formation of metavanadate which finally participates in the precipitation reaction (88).

$$2Na_3VO_4 + 2NH_4Cl + H_2O \rightarrow Na_4V_2O_7 + 2NaCl + 2NH_4OH \quad [16]$$

$$Na_4V_2O_7 + 2NH_4Cl + H_2O \rightarrow 2NaVO_3 + 2NaCl + 2NH_4OH \quad [17]$$

Ammonium metavanadate decomposes to vanadium pentoxide at 500°C (Eq.[18]).

$$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3(g) + H_2O \quad [18]$$

To avoid the formation of mixed tetravalent and pentavalent vanadium oxides in the final product, the ammonium metavanadate is heated in excess air and the temperature is raised slowly. The decomposition occurs in two steps (81). At 225 to 300°C, partial decomposition to ammonium trivanadate occurs, Eq.[19].

$$6NH_4VO_3 \rightarrow 2NH_4V_3O_8 + 4NH_3 + 2H_2O \quad [19]$$

Temperatures of 450°C or greater are required for the final de-ammoniation, Eq.[20].

$$2NH_4V_3O_8 \rightarrow 3V_2O_5 + 2NH_3(g) + H_2O \quad [20]$$

III. EXTRACTION OF VANADIUM FROM SUNCOR FLY ASH BY THE SODIUM CHLORIDE ROAST PROCESS

A. Experimental

Materials

A 20 kg sample of Suncor fly ash obtained in May 1980 was used throughout the experimental work unless otherwise indicated. Samples obtained in July 1977 and March 1982 were occasionally used for comparison. The fly ash was used both "as-received" and "carbon-free". "Carbon-free" fly ash was obtained by ashing to constant weight at 500°C.

Deionized water and reagent grade chemicals were used throughout.

Analytical Methods

"Carbon-free" fly ash was used in the determination of the elemental composition of Suncor fly ash to avoid the difficulties associated with the analysis of inorganics in carbon containing materials. Griffin showed that vanadium and other elements are not lost during ashing at 500°C by comparing neutron activation analysis of "as-received" fly ash with wet chemical analysis of "carbon-free" fly ash (5).

The elemental composition of "carbon-free" Suncor fly ash was determined by two different methods: the lithium metaborate fusion method, and the acid digestion method. In the lithium metaborate fusion method (ASTM D3682-78)

(Alberta Research Council Chemistry Analytical Services Laboratory), the ash was fused with lithium metaborate ($LiBO_2$) at 1000°C in platinum crucibles. The fusate was dissolved in dilute hydrochloric acid, and the resulting solution analyzed using a Bausch and Lomb Model 34000 inductively-coupled plasma spectrometer (ICP). In the acid digestion method, the ash was dissolved in concentrated hydrofluoric acid and aqua regia at 110°C in a Parr bomb containing a teflon liner (Parr Instrument Co., Moline, Ill.) (89, 90). The elevated temperature attained in the Parr bomb aids in complete dissolution of the sample. Boric acid was added to the digest solutions to complex the fluoride and the solutions were submitted for analysis by ICP (Alberta Research Council Chemistry Analytical Services Laboratory).

The ICP analyses of the acid digests and the leachates (see below) were checked by including standard solutions with the samples submitted for analysis. Standards were prepared which contained vanadium, nickel, iron, sodium, calcium, sulfur, silicon, and aluminum at concentrations of 10, 100, or 500 ppm, depending upon the concentration expected in the test solutions. The standards contained single elements or mixtures of elements. Matrix effects, if present, could not be discriminated from the random error associated with multiple analyses of a standard solution containing a single element.

Suncor fly ash "as-received" was ashed at 500°C to constant weight. The associated weight loss is reported as percent carbon in the fly ash since the weight loss was primarily due to the combustion of unburned carbon. The fly ash "as-received" was also analyzed for sulfur using method ASTM D3177-75. In this method, the sample is burned at 1000°C in a stream of oxygen which is subsequently passed through a hydrogen peroxide solution. The sulfur dioxide produced from the combustion of the sample is converted to sulfuric acid which is titrated with standardized base.

Roasting

Suncor fly ash was mixed with sodium chloride and roasted in a vessel composed of stabilized zirconia or porcelain (Coors). Porcelain boats 10 cm in length were placed in a horizontal tube furnace. Porcelain crucibles, zirconia plates, and zirconia crucibles were placed in a muffle furnace. These materials were chemically inert and relatively resistant to thermal shock. Quartz was used initially but it corroded rapidly when sodium chloride was present. The vessels were inserted slowly (1 to 2 min) into a furnace preheated to the roasting temperature to minimize the possibility of shatter from thermal shock. After roasting the required length of time, the samples were slowly withdrawn from the furnace and cooled to room temperature. The solid was then pulverized with a mortar and pestle.

Leaching

The extraction of vanadium and other elements was determined by leaching 1 g of the roast with 5 ml of water in 30 ml polyethylene bottles placed in a temperature controlled shaker bath at 95°C. After 1 hr, the slurry was filtered through a Millipore membrane filter (0.45 μm) and the solid washed with four 5-ml aliquots of deionized water. The filtrate was diluted to 100 ml and analyzed by ICP. The total concentration of vanadium and other elements in the roast were determined by the "acid digestion" method.

B. Chemical Analysis and Characterization

Elemental Analysis

The average of duplicate analyses of May 1980 Suncor fly ash is shown in Table 1. The results obtained by the lithium metaborate fusion method and the acid digestion method showed good agreement.

The analysis of three different samples of Suncor fly ash by the lithium metaborate fusion method is shown in Table 2. Also shown is an analysis reported by Griffin (5) for the 1977 sample. The concentrations of vanadium, nickel and silicon in the three samples of ash ("carbon-free" basis) taken over a period of five years is relatively constant. The variability in the iron concentration may reflect incorporation of scale into the coke from the walls of the delayed cokers. The unburned carbon content of the

Table 1. Elemental Analysis of May 1980 Suncor Fly Ash ("Carbon-Free" Basis)

ELEMENT	LITHIUM METABORATE FUSION METHOD (wt%)	ACID DIGESTION METHOD (wt%)
V	3.2	3.1
Ni	1.3	1.3
Fe	5.6	5.3
Ti	2.1	ND[1]
Si	20.7	19.2
Al	13.4	13.3
Ca	1.1	1.1
S	0.3	0.9
Na	0.5	0.4
Mg	0.8	ND

[1]Not determined.

Table 2. Elemental Analysis of Three Samples of Suncor Fly Ash

	SAMPLING DATE			
	July 1977	July[1] 1977	May 1980	March 1982
"AS-RECEIVED" BASIS				
sulfur (%)	3.0	-	2.3	2.4
carbon (%)	59.1	47.8	41.0	42.9
"CARBON-FREE" BASIS (%)				
Si	19.7	20.6	20.6	19.8
Al	13.3	16.1	13.4	13.9
V	3.2	3.7	3.2	3.8
Ni	1.3	1.4	1.3	1.5
Fe	11.9	6.8	5.6	11.4
Ti	2.8	3.8	2.1	2.3
Na	0.4	1.6	0.5	0.4
Mg	0.9	0.8	0.8	0.8
Ca	1.7	0.2	1.1	1.0
S	0.2	-	0.3	0.3

[1]Analysis reported by Griffin (5)

fly ash samples (40 to 60%) is a function of boiler operation during combustion of the pulverized coke. The unburned carbon accounted for the brownish-black appearance of the "as-received" fly ash which turned reddish-brown on ashing. The "as-received" fly ash also contained 2 to 3% sulfur, 95% of which is lost during ashing at 500°C.

Electron Spin Resonance Spectroscopy

Electron spin resonance spectroscopy (ESR) was used to try to determine the oxidation state of vanadium and iron present in the fly ash. Vanadium in the tetravalent or bivalent state and iron in the trivalent state produce characteristic ESR spectra as the metal ions in these respective oxidation states contain single unpaired electrons. Analysis of the fly ash "as-received" and "carbon-free" by a Varian E-102 X band spectrometer gave no signal for vanadium and only a weak signal for iron. Vanadium is likely present in the pentavalent state, as the trivalent state would only exist under highly reducing conditions (12).

X-Ray Diffraction Analysis

Powder diffraction patterns were obtained on a Philips PW 1380 Diffractometer equipped with a horizontal goniometer. The samples were scanned at 0.5 °/min from 4 to 30° using copper K-alpha radiation and a nickel filter. Powdered reagent grade sodium chloride was used as a

reference material. Compounds were identified by either the Hanawalt search method (91) or by matching the pattern of the unknown with tabulated patterns. A match with a detailed pattern published in the ASTM Powder Diffraction File (92) was considered confirmation of the presence of a compound.

The powder diffraction patterns obtained for Suncor fly ash either "as-received" or "carbon-free" were similar. They showed a number of small broad peaks characteristic of samples containing a large amount of amorphous material. Analysis of the pattern identified mullite ($Al_6Si_2O_{16}$) with all major peaks present. No other compounds could be identified. The presence of mullite is reasonable as the fly ash is formed from the entrained solids in Athabasca bitumen (0.05 to 0.10 %) which are a mixture of quartz, kaolinite, illite, and dolomite (93). Kaolinite converts to metakaolinite at 500°C and to mullite at 1200°C (94). Other aluminosilicates or mixtures of silica and alumina also can react to form mullite at combustor temperatures (94).

Scanning Electron Microscopy

Fly ash was slurried with acetone and a drop of the mixture placed on an aluminum stub coated with silver paste. After the acetone had completely evaporated, the specimen was coated with gold for detailed visual examination, or with carbon for both visual and chemical examination. The samples were viewed in an ISI-60 scanning electron microscope (SEM) operated at 30 KeV. The microscope was

equipped with a Tracor Northern Model TN-1710 energy dispersive X-ray analyzer (EDA) which gave a semiquantitative elemental analysis of the total specimen or of structures on the specimen surface. Elements of atomic number 10 (neon) and greater could be detected.

Suncor fly ash "as-received" consisted of the characteristic aluminosilicate spheres and porous char particles (Plate 1). The largest aluminosilicate spheres in the photograph are about 10 μm in diameter, with many being 2 μm or less.

When fly ash contains appreciable unburned carbon, the char particles are normally found in the large size fractions of the fly ash (95). Therefore, for closer examination of the char particles, the fly ash was screened with a 200 mesh sieve. The +200 mesh material (>75 μm) was black and the weight loss (percent unburned carbon) upon ashing at 500°C was 85.9%. At low magnification the +200 mesh particles appeared porous and irregularly shaped (Plate 2). Progressive magnification of the surface of the particles showed that numerous micron-sized spheres were embedded in the pore structure (Plate 3 and Plate 4). This explains why the average particle size in Suncor fly ash "as-received" is much larger than for "carbon-free" fly ash, 15.7 μm versus 3.8 μm respectively (5, 37). In the "carbon-free" fly ash the large char structures are absent, and the embedded micron-sized aluminosilicate spheres have been freed.

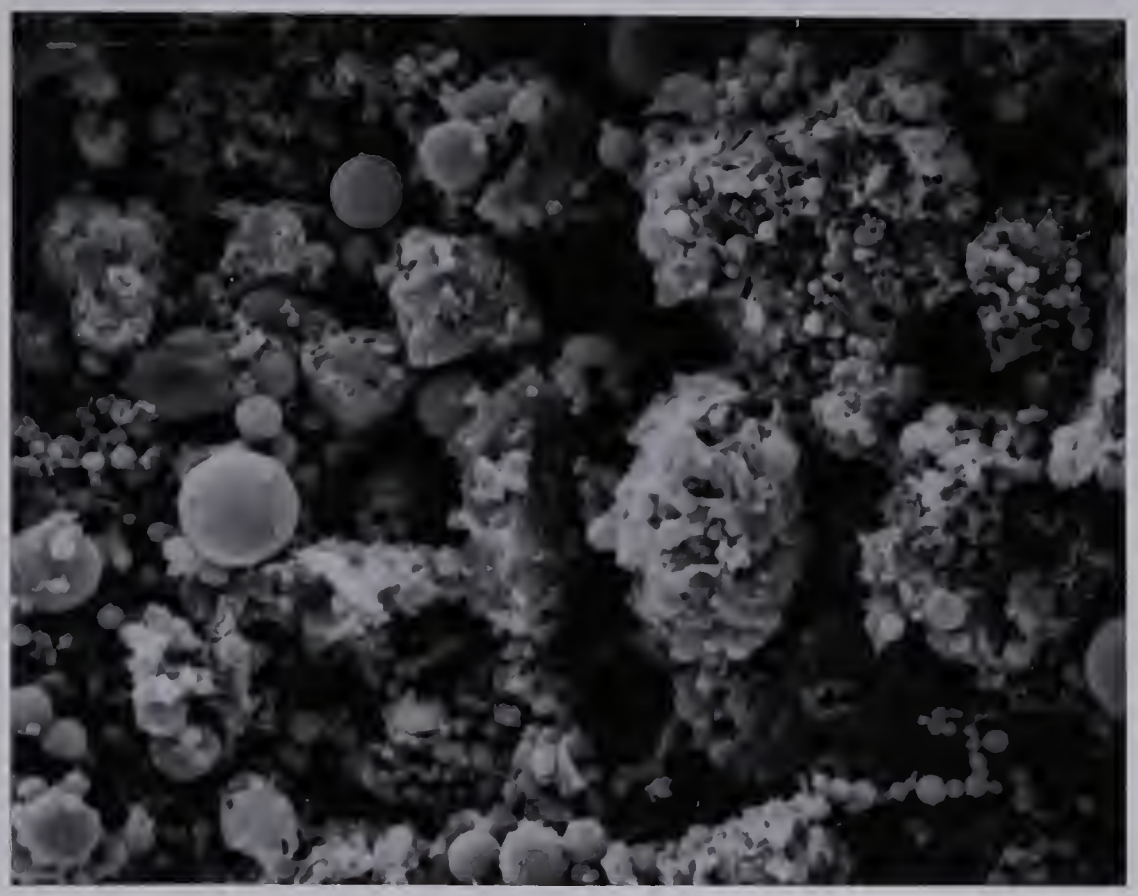

Plate 1. Suncor Fly Ash "As-Received" (770X)
Right hand marker = 10 μm

Plate 2. Char Particles (250X)
Right hand marker = 10 μm

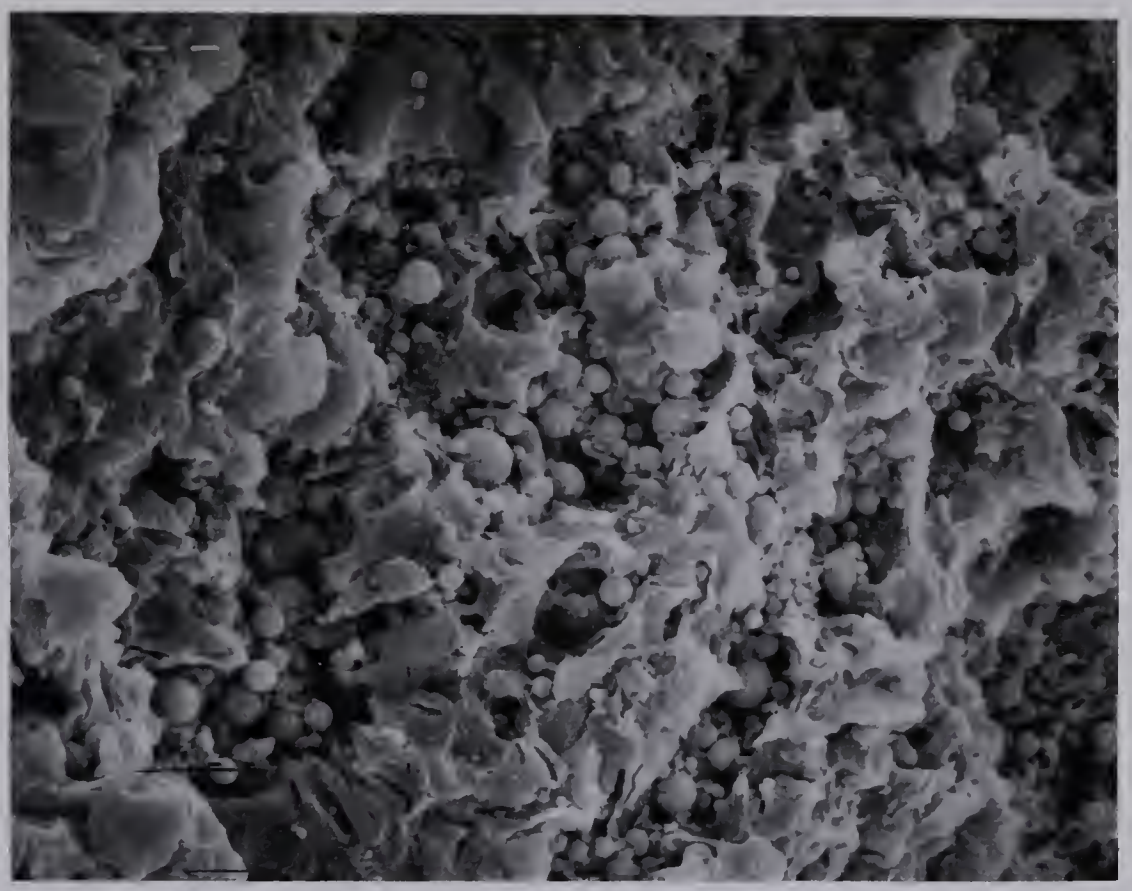

Plate 3. Magnification of the Surface of a Char Particle (2500X)
Right hand marker = 1 μm

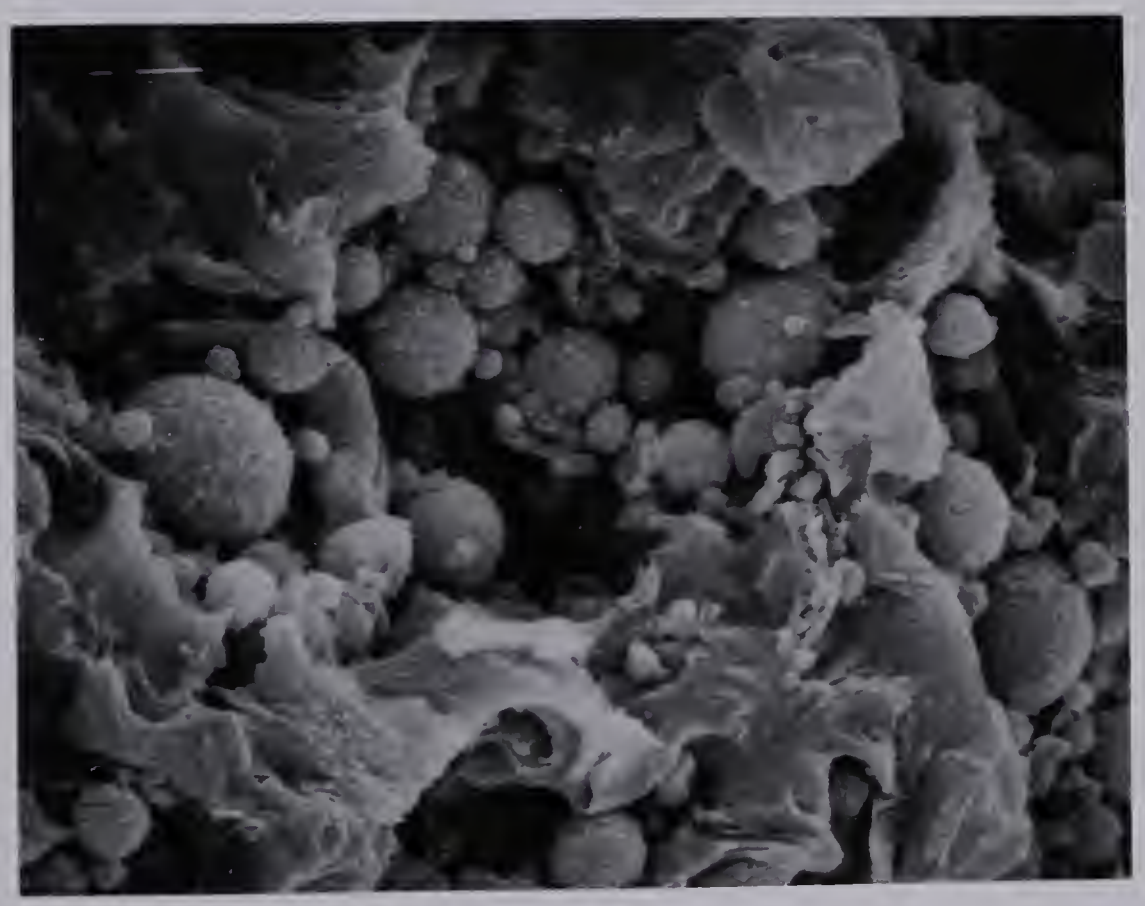

Plate III.4 Magnification of the Surface of a Char Particle (6000X)
Right hand marker = 1 μm

The crystalline particles found by other investigators (5, 37, 95) were not observed, although some particles contained striations (Plate 5). Broken cenospheres (hollow spheres) were common in the sample (Plate 6). Occasional pleurospheres (95) which are large spheres with entrapped spheres were observed (Plate 7). However, the "pleurospheres" may be broken cenospheres which later became filled with smaller spheres.

Chemical analysis using the X-ray dispersive analyzer confirmed that the spheres consisted of an aluminosilicate containing low concentrations of vanadium, nickel, titanium, iron, and potassium. The porous particles contained sulfur in appreciable concentration, the signals for all other elements being very weak. The observations of Suncor fly ash in this study are generally consistent with previous studies (5, 36), including those for fly ash produced during the combustion of pulverized coal in power generating plants (38, 39).

Fusibility of Ash Analysis

The fusibility-of-ash test is an empirical test method developed to predict the temperature at which the ash in coal or coke will become fluid during combustion in boilers. "Carbon-free" Suncor fly ash and ash obtained by ashing pulverized Suncor coke at 500°C were submitted to Chemical and Geological Laboratories (Edmonton, Alberta) for analysis according to ASTM M-1857. This method consists of heating

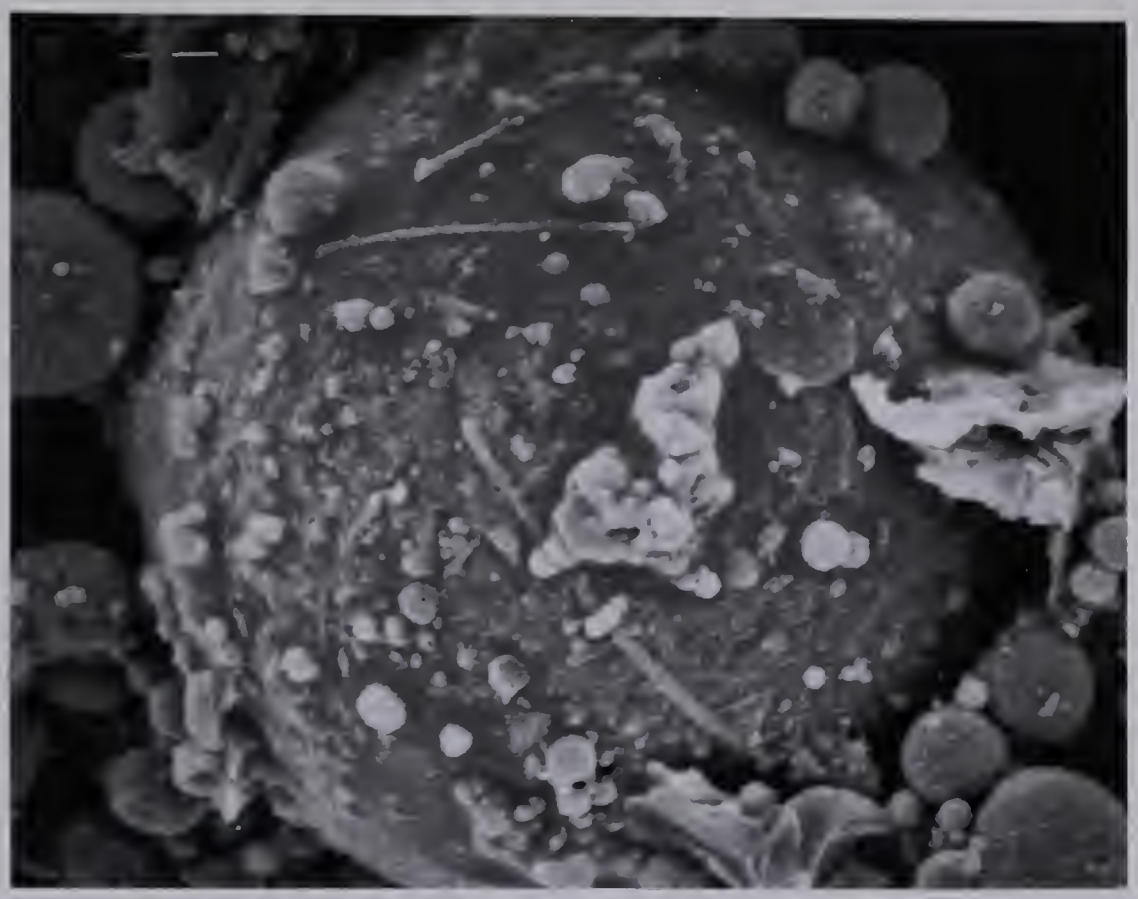

Plate 5. Sphere Showing Striations (4200X)
Right hand marker = 1 μm

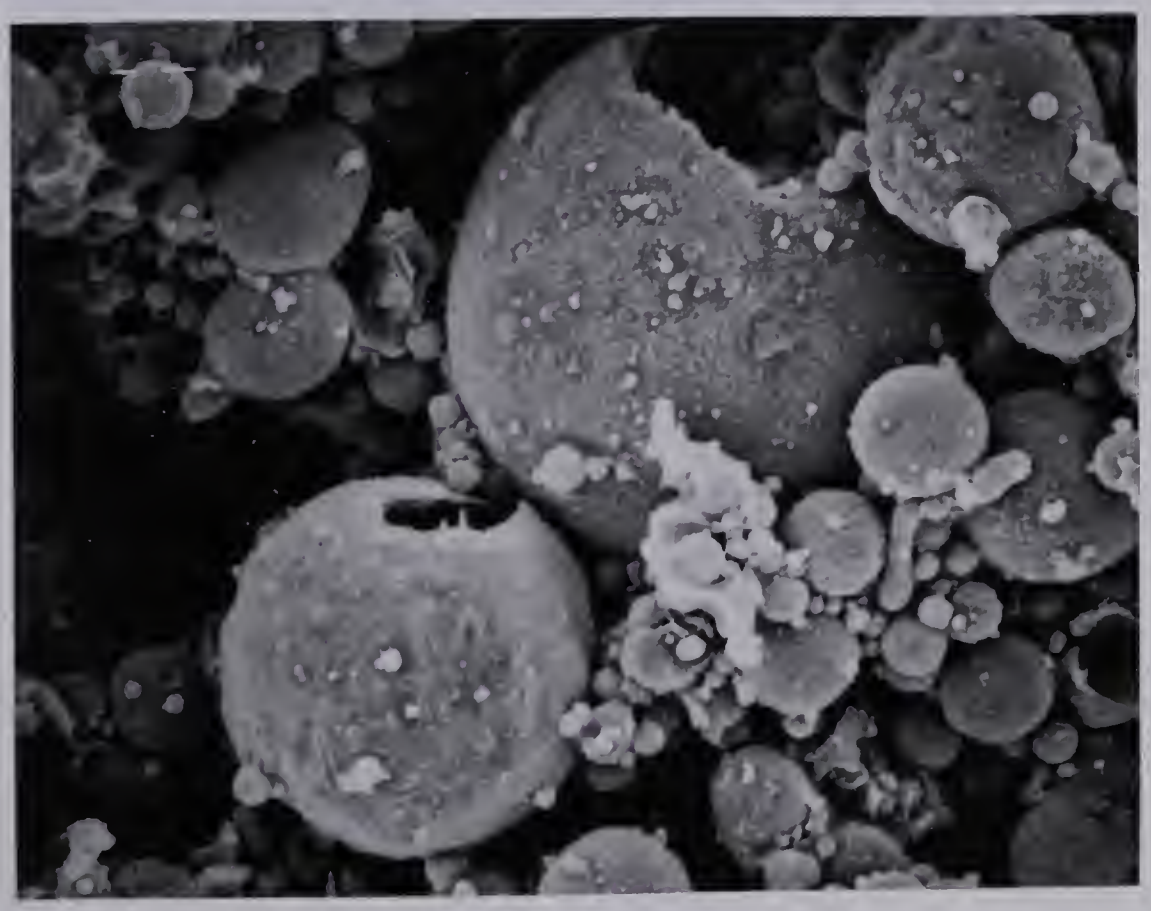

Plate 6. Broken Cenosphere (3000X)
Right hand marker = 1 μm

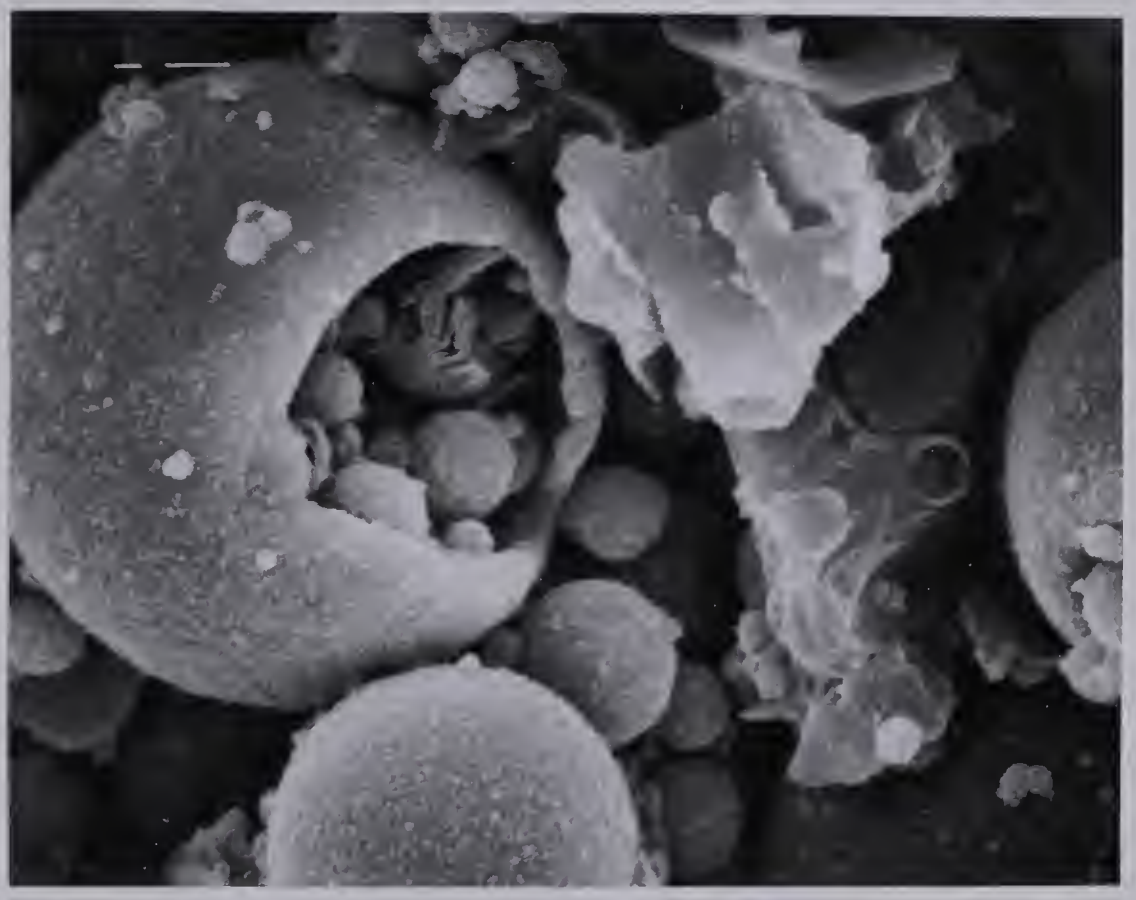

Plate 7. Pleurosphere (6000X)
Right hand marker = 1 μm

cones of fly ash at a programmed rate and observing the temperature at which the cones attain the following configurations: initial deformation temperature; softening temperature; hemispherical temperature; fluidity temperature. Tests are run in both an oxidizing atmosphere (air) and a reducing atmosphere (60% CO, 40% CO_2) because the fluxing of aluminosilicates by substances such as iron oxide varies depending upon their oxidation state.

The results show (Table 3) that Suncor fly ash did not reach fluidity at 1450° C, the maximum temperature reached in the test method. However, Suncor coke ash became fluid at 1345°C in an oxidizing atmosphere. This indicates that the inorganics in the coke are irreversibly converted to high melting compounds such as mullite[1] during combustion of the coke in Foster-Wheeler boilers.

C. Preliminary Roasting Experiments

Industrial roasting operations are conducted in multiple hearth roasters, rotary kilns, fluidized bed reactors, or flash-suspension systems. The use of fluidized bed roasting or flash-suspension roasting is becoming more common because of the superior heat transfer and temperature control, better solid/gas mixing, and higher ore through-put associated with these methods (96). In Griffin's study the fly ash/sodium chloride mixture was roasted in a boat placed in a tube furnace and the charge was heated from 25 to 905°C

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[1]The melting point of mullite is 1850°C.

Table 3. Fusibility of Ash Analysis

	IT °C	ST °C	HT °C	FT °C
Suncor Fly Ash ("carbon-free")				
ATMOSPHERE:				
Oxidizing	1410	1440	1450+	1450+
Reducing	1400	1450+	1450+	1450+
Suncor Coke Ashed at 500° C to Constant Weight				
ATMOSPHERE:				
Oxidizing	1305	1320	1330	1345
Reducing	1195	1230	1250	1280

IT- Initial Deformation Temperature: cone tip rounded
ST- Softening Temperature: cone fused to a hemisphere, hemisphere height equals diameter
HT- Hemispherical Temperature: cone fused to a hemisphere, hemisphere height equals one half the diameter
FT- Fluid Temperature: liquid spreads in a thin film

over a two hour period (5). In contrast to fluidized bed or flash-suspension roasting, there was no gas/solid mixing and the feed was heated slowly, rather than "instantaneously", to the roasting temperature.

In an attempt to better approximate industrial roasting conditions, and to increase gas/solid contact, a 3 mm layer of the fly ash/sodium chloride mixture was roasted on a stabilized zirconia plate using Griffin's optimized roasting conditions (14% sodium chloride, 905°C, 6 hr). However, the vanadium extraction obtained by hot water leaching was 10% compared to the 95% reported by Griffin. By varying the roasting temperature, the extraction of vanadium was increased to a maximum of 30% at 800°C (Figure 2).

For comparison, the fly ash/sodium chloride mixture was also roasted in a boat in a tube furnace using Griffin's conditions, but the extraction of vanadium was only 30%. One of the differences in the conditions used in the two studies was that the ash had been heated from room temperature to roasting temperature in one hour, compared to two hours in the previous study. Investigation of the effect of the warmup time showed that the vanadium recovery increased from 30% for a one hour warmup time to 60% for a three hour linear warmup time (Table 4). Using a three hour warmup time, the roasting temperature was varied but the vanadium extraction did not increase any further (Figure 3). Mass balance calculations indicated that there was no detectable loss of vanadium through the formation of volatile

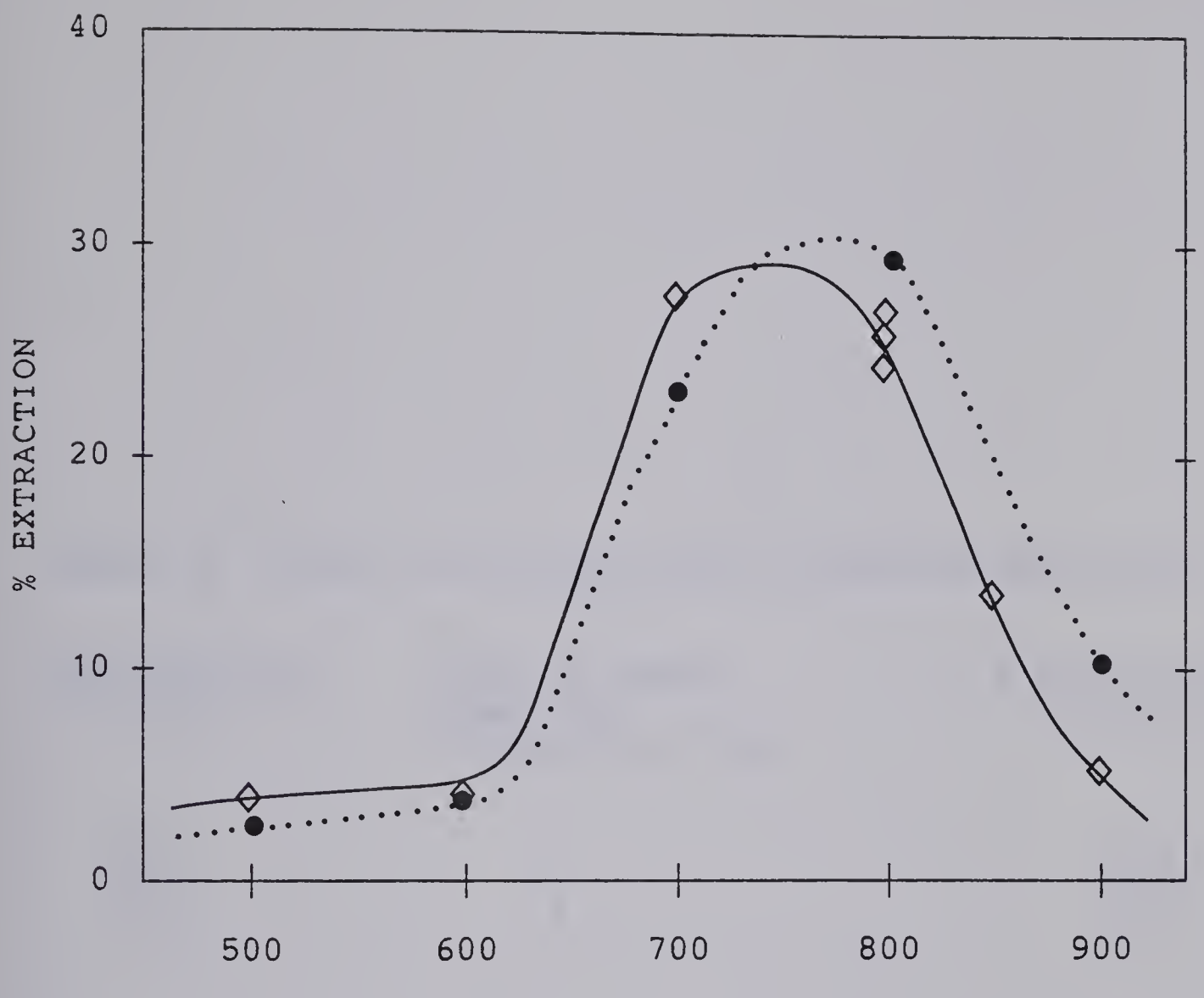

Figure 2. Suncor Fly Ash Roasted With 15% Sodium Chloride on a Stabilized Zirconia Plate.
◇ 2 hr, ● 6 hr.

Table 4. Effect of Warmup Time on Vanadium Extraction

Heating Rate (°C/min)	Time to Reach Roasting Temperature (hr)	% Extraction of Vanadium
15.0	1	30.4
8.0	2	43.8
5.0	3	59.7

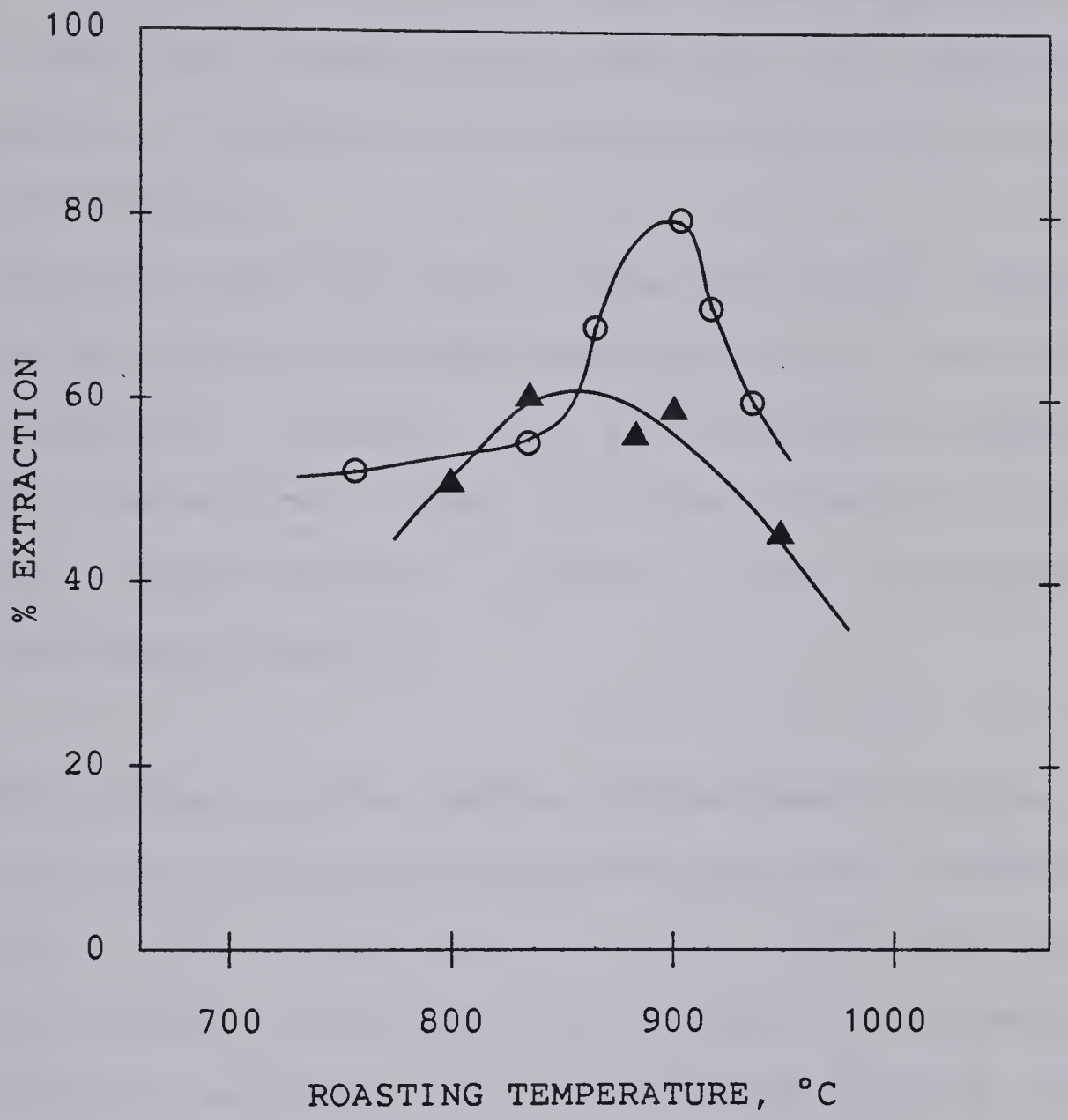

Figure 3. Suncor Fly Ash Roasted with Sodium Chloride in a Ceramic Boat Placed in a Tube Furnace.
▲ This study
○ Griffin's study (5)

chlorides. There was little change in the extraction when the 1977 or 1982 samples of Suncor fly ash were used in place of the 1980 sample. An additional interesting observation was made. A white solid was deposited on the ends of the tube furnace during roasting. The deposit was identified as sodium chloride by chemical analysis and by X-ray diffraction.

The major conclusion from these preliminary experiments was that the sodium chloride roast process is more complex than originally thought, and that factors in addition to roasting temperature, time, and the amount of sodium chloride significantly affect the formation of water-leachable vanadium.

D. Factors Affecting the Sodium Choride Roast Process

From the preliminary experiments and from observations reported in the literature, it was concluded that the following factors could potentially affect the formation of water-soluble vanadium during the sodium chloride roasting of Suncor fly ash:

1. The rate at which the charge is heated to the roasting temperature;
2. The rate at which the roast is cooled. Slow cooling could result in the formation of water-insoluble "bronzes" (54, 55);
3. The partial pressure of oxygen in the roasting atmosphere. The vanadium extraction was very low when

the roasting was done in an inert (nitrogen) atmosphere or a reducing (hydrogen) atmosphere (5);

4. The partial pressure of water in the roasting atmosphere. A low moisture level in the roast atmosphere could result in low vanadium extraction since water is a reactant in one of the sodium chloride roast reactions (Eq.[1]). Alternatively, water could have an adverse effect by reacting with silica in the water glass reaction (Eq.[6]) to form a glass which could entrap the vanadium;
5. The loss of sodium chloride through volatilization. At 900° C, the vapor pressure of sodium chloride is 4 torr (97);
6. The presence of unburned carbon could be detrimental (25, 52);
7. The flow rate of roaster gases through or over the fly ash bed. The supply of the gaseous reactant (water), the removal of the gaseous products (chlorine or hydrogen chloride), and the removal of volatile sodium chloride reagent would all be affected by flow rate;
8. The pH of the leachate. The extraction could be higher in acidic or basic solutions (5, 37);
9. The roasting temperature;
10. The roasting time;
11. The amount of sodium chloride added to the fly ash.

To determine which of these factors had the greatest effect on the sodium choride roast/hot-water leach process,

a Plackett-Burman screening design experiment was carried out.

E. Plackett-Burman Screening Design Experiment

Normally only three to five factors have a significant effect on a chemical process (98). Possible factors include temperature, reactor type, time, pretreatment procedure, and so on. The Plackett-Burman screening design is one of several statistical techniques by which the significant factors can be determined from a large number of candidate factors (98, 99, 100, 101). Each factor is assigned a high (+) and low(-) level. A quantitative variable, such as time, could be set to 5 minutes (-) and 60 minutes (+). A qualitative variable, such as pretreatment, could be arbitarily assigned pretreatment #1 (-) and pretreatment #2 (+). Depending upon the number of variables to be screened and the confidence level desired, the experiment is run according to the appropriate Plackett-Burman design. The design consists of a series of trials in which the factors are set at predetermined high(+) or low(-) levels. After the experimental results are obtained, statistical calculations are used to determine which of the factors significantly affect the process at various confidence levels. Additional details on this design can be found in the APPENDIX.

Nine factors were screened for the sodium chloride roast process (Table 5). Heating rate was excluded as a factor because it is not independent of roasting time or

Table 5. Variables for the Plackett-Burman Screening Design Experiment and Assigned High(+) and Low(-) Levels

VARIABLE	HIGH LEVEL(+)	LOW LEVEL(-)
Partial pressure of water vapor(torr)	23.7	2×10^{-5}
Ash bed depth (cm)	2	0.8
Carbon content of ash	nil (decarbonized)	41.0% ("as-received")
Time to cool roasted solid (hr)	slow cool 6 to 8	quench 0.5
Gas flow rate: ml/min Reactor volumes/min	1000 0.5	200 0.1
Roasting time (hr)	4	1
Roasting temperature (°C)	900	700
Mole ratio Na/V in ash	6.9	2.3
Roasting Atmosphere	air	technical nitrogen 0.1% O_2

temperature. Leachate pH was excluded because of the economic advantage of leaching with water.

Table 6 and Table 7 show the twenty-run Placket-Burman design used and the conditions for each of the twenty trials. In each trial, the fly ash/sodium chloride mixture was roasted in a porcelain boat inserted directly into a tube furnace at roasting temperature. The tube furnace was fitted with a gas inlet at one end and was flushed prior to introduction of the boat with either air (wet or dry) or nitrogen (wet or dry) as dictated by the design. The flow rate of gas was set with flow controllers. At the completion of roasting, the roasted solid was either quenched by immediately withdrawing the boat from the furnace, or cooled slowly over 6 to 8 hr by turning the furnace off without removing the boat.

In the statistical analysis shown in Tables 6 and 7 the UNASSIGNED FACTOR EFFECTS were used to calculate the experimental response error. The response error, that is [MIN], was used to test each of the nine factors for their significance in affecting the vanadium extraction. At the 95% confidence level, roast atmosphere was statistically significant, although the FACTOR EFFECT was just marginally above the minimum required for significance. At the 90% confidence level three factors had a significant effect: roasting atmosphere, the amount of sodium chloride added to the ash, and preroasting. Again the magnitudes of the FACTOR EFFECTS were only slightly above the minimum value required

Table 6. Twenty-Run Plackett-Burman Screening Design: Factor Assignments, Results, and Statistical Calculations

Factor		X1	X2	X3	X4	X5	X6	X7	X8	X9
Trial	%VANADIUM EXTRACTION	H_2O IN GAS (torr)	BED DEPTH (cm)	PRE-ROAST	COOL RATE	FLOW RATE (ml/min)	ROAST TIME (hr)	ROAST TEMP (°C)	% NaCl	ROAST ATMOSPHERE
1	0.6	23.7	2.0	no	fast	200	4	900	6.9	N_2
2	6.7	23.7	0.8	no	slow	200	4	900	2.2	air
3	9.7	10^{-5}	0.8	yes	slow	200	4	700	6.9	N_2
4	11.8	10^{-5}	2.0	yes	slow	200	1	900	2.2	air
5	9.3	23.7	2.0	yes	slow	1000	4	700	6.9	N_2
6	7.6	23.7	2.0	yes	fast	200	1	900	2.2	N_2
7	2.3	23.7	2.0	no	slow	1000	4	700	2.2	N_2
8	8.3	23.7	0.8	yes	fast	200	1	700	2.2	N_2
9	0.1	10^{-5}	2.0	no	slow	1000	1	700	2.2	air
10	12.9	23.7	0.8	yes	fast	1000	1	700	6.9	air
11	0.1	10^{-5}	2.0	no	fast	1000	1	900	6.9	N_2
12	7.8	23.7	0.8	no	fast	1000	4	900	2.2	air
13	23.4	10^{-5}	0.8	no	fast	200	4	700	6.9	air
14	1.1	10^{-5}	0.8	no	slow	200	1	900	6.9	N_2
15	3.3	10^{-5}	0.8	yes	slow	1000	4	900	2.2	N_2
16	8.5	10^{-5}	2.0	yes	fast	200	4	700	2.2	air
17	1.3	23.7	2.0	no	slow	200	1	700	6.9	air
18	32.0	23.7	0.8	yes	slow	1000	1	900	6.9	air
19	88.1	10^{-5}	2.0	yes	fast	1000	4	900	6.9	air
20	2.3	10^{-5}	0.8	no	fast	1000	1	700	2.2	N_2
Sum+		88.8	129.7	191.6	77.6	79.1	159.6	159.2	178.5	192.5
Sum-		148.5	107.6	45.7	159.7	158.1	77.6	78.1	58.7	44.7
Overall		237.2	237.2	237.2	237.2	237.2	237.2	237.2	237.2	237.2
Difference		-59.8	22.1	145.9	-82.1	-79.0	82.0	81.1	119.8	147.8
FACTOR EFFECT		-5.9	2.2	14.6	-8.2	-7.9	8.2	8.1	12.0	14.8

Standard deviation of unassigned factor effects = 6.7
[MIN] = t x standard deviation of unassigned factor effects
[MIN] = 2.23 x 6.7 = 14.9 95% confidence limit
[MIN] = 1.81 x 6.7 = 12.2 90% confidence limit
[MIN] = 0.7 x 6.7 = 4.7 50% confidence limit

Table 7. Twenty-Run Plackett-Burman Screening Design: Unassigned Factors and Calculation of Experimental Error

TRIAL	%VANADIUM EXTRACTION	UNASSIGNED VARIABLES									
		x10	x11	x12	x13	x14	x15	x16	x17	x18	x19
1	0.6	+	-	+	-	-	-	-	+	+	-
2	6.7	-	+	-	-	-	-	+	+	-	+
3	9.7	+	-	-	-	-	+	+	-	+	+
4	11.8	-	-	-	-	+	+	-	+	+	-
5	9.3	-	-	-	+	+	-	+	+	-	-
6	7.6	-	-	+	+	-	+	+	-	-	+
7	2.3	-	+	+	-	+	+	-	-	+	+
8	8.3	+	+	-	+	+	-	-	+	+	+
9	0.1	+	-	+	+	-	-	+	+	+	+
10	12.9	-	+	+	-	-	+	+	+	+	-
11	0.1	+	+	-	-	+	+	+	+	-	+
12	7.8	+	-	-	+	+	+	+	-	+	-
13	23.4	-	-	+	+	+	+	-	+	-	+
14	1.1	-	+	+	+	+	-	+	-	+	-
15	3.3	+	+	+	+	-	+	-	+	-	-
16	8.5	+	+	+	-	+	-	+	-	-	-
17	1.3	+	+	-	+	-	+	-	-	-	-
18	32.0	+	-	+	-	+	-	-	-	-	+
19	88.1	-	+	-	+	-	-	-	-	+	+
20	2.3	-	-	-	-	-	-	-	-	-	-
Sum+		71.8	132.7	91.8	150.3	104.6	80.2	63.7	76.5	142.7	178.3
Sum-		165.5	104.5	145.4	86.9	132.7	157.0	173.5	160.7	94.5	58.9
Overall		237.2	237.2	237.2	237.2	237.2	237.2	237.2	237.2	237.2	237.2
Difference		-93.7	28.2	-53.5	63.5	-28.1	-76.8	-109.8	-84.2	48.1	119.4
UNASSIGNED FACTOR EFFECT		-9.4	2.8	-5.4	6.4	-2.8	-7.7	-11.0	-8.4	4.8	1.2

S(fe), standard deviation of unassigned factor effects = 6.7

for significance. Comparison of the ASSIGNED and UNASSIGNED FACTOR EFFECTS showed that they were of similar magnitudes, indicating the presence of strong factor interactions. This meant that the [MIN] value was an overestimation of response error as it includes interaction effects in addition to response error (102).

Consequently replication of Trial 19 was used to calculate the response error and factor significance using a method described by Murphy (102). In this method a "confidence interval" is calculated for each factor. If the confidence interval does not include zero, the effect is significantly different from zero at the given confidence level.

The replication of Trial 19 gave 88.1% 90.2%, 84.1% and 89.3% vanadium extraction. The standard deviation of these values is 2.69. The confidence interval was calculated from the equation:

$$\text{confidence interval} = \text{FACTOR EFFECT} \pm ts/(N/4)^{1/2}$$

where

t = Student's t statistic

s = standard deviation of the replicates

N = the number of trials in the design

The number of degrees of freedom is (r - 1) were r is the number of replicates. The confidence intervals at the 99% and 95% confidence levels are shown in Table 8. At the 99% level, seven of the nine factors are significant and at the 95% confidence level, eight out of nine. Of the ten

Table 8. Confidence Intervals for the Screening Design Experiment

FACTOR	CONFIDENCE INTERVAL			
	95%		99%	
Partial pressure of water vapor	-12.9	1.1	-9.7	-2.1
Ash bed depth	-4.8	9.2	-1.6	6.0
Carbon content of ash	7.6	21.6	10.8	18.4
Time to cool roast	-15.2	-1.2	-12.0	-4.4
Gas flow rate	-14.9	-0.9	-11.7	-4.1
Roast time	1.2	15.2	4.4	12.0
Roasting temperature	1.1	15.1	4.3	11.9
Mole ratio Na/V	5.0	19.0	8.2	15.8
Roasting Atmosphere	7.8	21.8	11.0	18.6

unassigned factors, four are significant at the 99% confidence level and seven at the 95% level. This analysis indicates almost all of the factors significantly affect the process and that strong factor interactions are present. Examination of the data supports the conclusion of the latter statistical analysis. Whereas the vanadium recovery was less than 10% in most of the trials, in Trial 13 and Trial 18 the extractions were 23.4% and 32.0%. Further, the specific combination of factor levels in Trial 19 resulted in 88.1% extraction.

Comparison of the factor levels in Trials 18 and 19 showed that in both cases the fly ash was decarbonized by preroasting at 500°C, the roasting atmosphere was air, the mole ratio of sodium chloride to vanadium was 6.9, the roasting temperature was 900° C, and the gas flow rate was 1000 ml/min. The decrease in vanadium recovery from 88.1 to 32.0% was attributed to the shorter roasting time, the slow cooling of the roasted solid, the reduced bed depth, or the presence of moisture in the roasting atmosphere. Analysis of the solid obtained in Trial 19 by X-ray diffraction indicated the presence of a sodium aluminosilicate, $NaAlSi_3O_8$. No vanadium compounds could be identified.

F. Follow-up Experiments and Discussion of the Sodium Chloride Roast Process

Additional experiments were carried out to learn more about the effects of the various factors because the results of the screening experiment were inconclusive. Using the conditions of Trial 19 as a reference, the factors were varied one at a time to their alternate levels. The results show that in each case, the vanadium extraction dropped (Table 9).

The detrimental effect of moisture is suprising because moisture is a reactant in the sodium chloride roast process. The fly ash mixture formed a particularly hard solid when roasted in a moist atmosphere, suggesting that the fly ash particles were partially fused, possibly by a glassy silicate. This, in turn suggests that water participates in a side reaction which results in reduced formation of water soluble vanadium. One possible reaction is the water glass reaction. The sodium silicate formed in this reaction may form a glassy phase which incorporates vanadium in a non-leachable form. Hydrolysis of sodium chloride to sodium hydroxide which subsequently reacts with silica to form sodium silicate is unlikely because the free energy of the hydrolysis reaction is 29.8 kcal/mole of sodium chloride (69).

The detrimental effect of decreasing the bed depth can be explained by increased loss of sodium chloride vapor. Decreasing the bed depth decreases the distance over which the vapor must diffuse before reaching the surface of the

Table 9. Determination of the Effect of the Various Factors on the Vanadium Extraction[1]

	%VANADIUM EXTRACTION	WATER in GAS (torr)	BED DEPTH (cm)	CARBON CONTENT	COOL RATE	FLOW RATE (ml/min)	ROAST TIME (hr)	ROAST TEMP (°C)	MOLE RATIO NaCl	ROAST ATMOSPHERE
TRIAL 19	88.1	10^{-8}	2.0	nil	fast	1000	4	900	6.9	air
FACTOR CHANGED										
Water in roast atmosphere	33.9	23.7	-	-	-	-	-	-	-	-
Bed depth	34.4	-	0.8	-	-	-	-	-	-	-
Cool rate of roasted solid	78.4	-	-	-	slow	-	-	-	-	-
Gas flow rate	83.8	-	-	-	-	200	-	-	-	-
Roast time	72.2	-	-	-	-	-	1	-	-	-
Roast atmosphere	82.4	-	-	-	-	-	-	-	-	N_2
Carbon content of ash	46.3	-	-	41.0%	-	-	-	-	-	-
Carbon content, roast atmosphere	0.1	-	-	41.0%	-	-	-	-	-	N_2
Carbon content, bed depth	28.6	-	0.8	41.0%	-	-	-	-	-	-
Carbon content, bed depth, gas flow rate	47.6	-	0.8	41.0%	-	200	-	-	-	-

[1]Dash indicates same conditions as in Trial 19.

bed where it is carried away in the flow of air. Reducing the air flow rate would be expected to increase vanadium extraction by further reducing the loss of sodium chloride vapor. This did not occur however, indicating that removal of gaseous products is also important. An optimum flow rate over the fly ash bed would represent a balance between the removal of end products and the retention of sodium chloride vapor.

The role of volatile sodium chloride in the sodium chloride roast reaction, Eq.[1] and Eq.[2], may have been overlooked in mechanistic and kinetic studies. The standard free energy of reaction of sodium chloride with vanadium pentoxide to form sodium metavanadate was calculated from the data tabulated by Barin and Knacke[1] (69). The standard free energy of reaction is positive throughout the temperature range of 400 to 1000°C when sodium chloride is treated as a liquid but is negative if sodium chloride is treated as a vapor (Figure 4). Similar results (Figure 5 and 6) are observed for the reactions in which sodium pyrovanadate and sodium orthovanadate form directly from sodium chloride and vanadium pentoxide.

However, these free energy calculations are for standard conditions in which chlorine and hydrogen chloride are present at 1 atm pressure and the liquid vanadium

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[1]Barin and Knacke (69) tabulated the free energy of formation of various inorganic compounds and the elements as a function of temperature (100° intervals). Similar data tables for vanadium compounds have been published by Mah (103). The free energies of reaction calculated from the data of the two sources agreed within 2 to 3 kcal/mole.

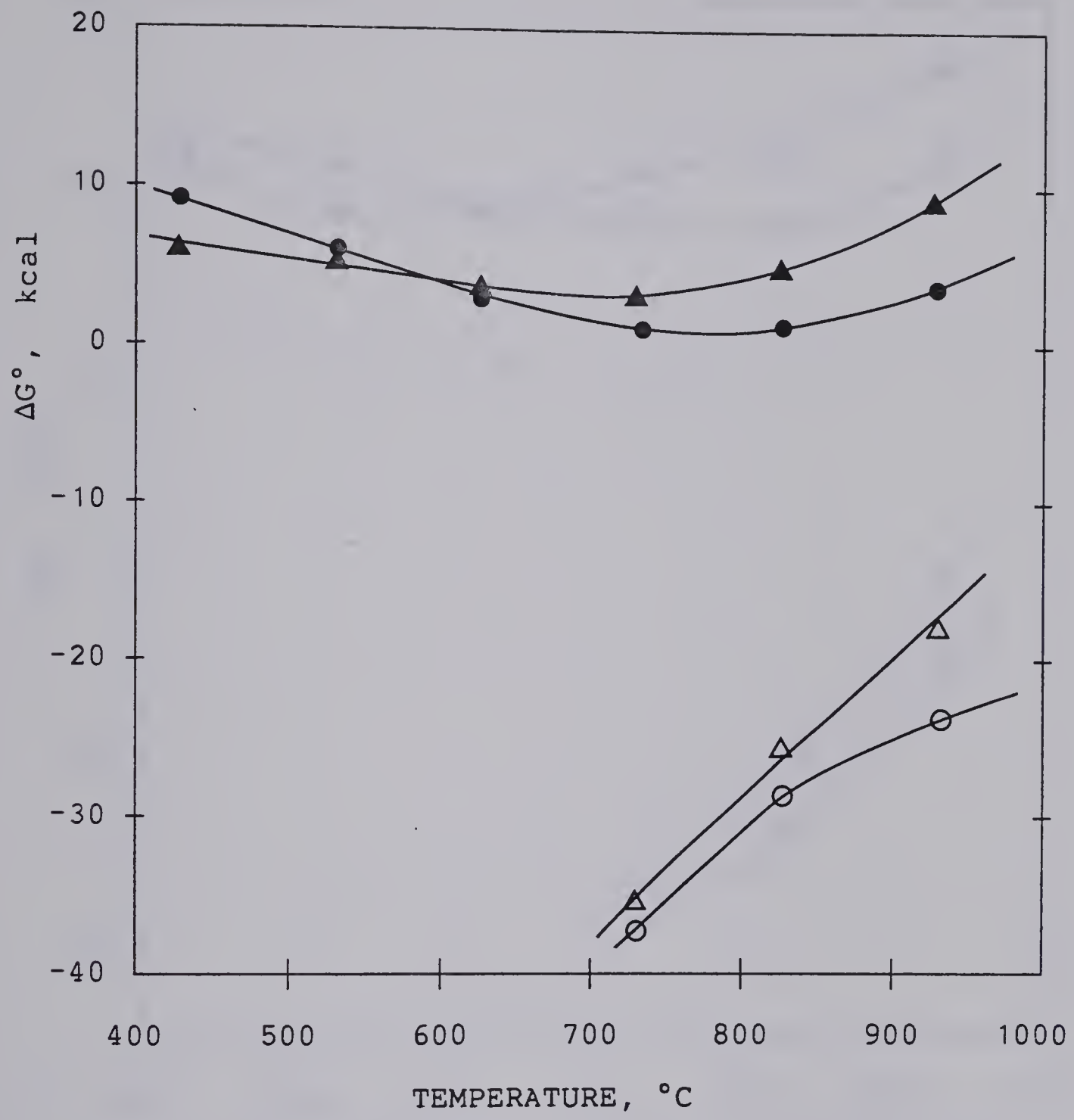

Figure 4. The Standard Free Energy of Reaction for the Formation of Sodium Metavanadate from Sodium Chloride and Vanadium Pentoxide.

▲ $2NaCl(l) + V_2O_5(s,l) + 1/2\ O_2 \leftrightarrow 2NaVO_3(s) + Cl_2$

△ $2NaCl(g) + V_2O_5(s,l) + 1/2\ O_2 \leftrightarrow 2NaVO_3(s) + Cl_2$

● $2NaCl(l) + V_2O_5(s,l) + H_2O \leftrightarrow 2NaVO_3(s) + 2HCl$

○ $2NaCl(g) + V_2O_5(s,l) + H_2O \leftrightarrow 2NaVO_3(s) + 2HCl$

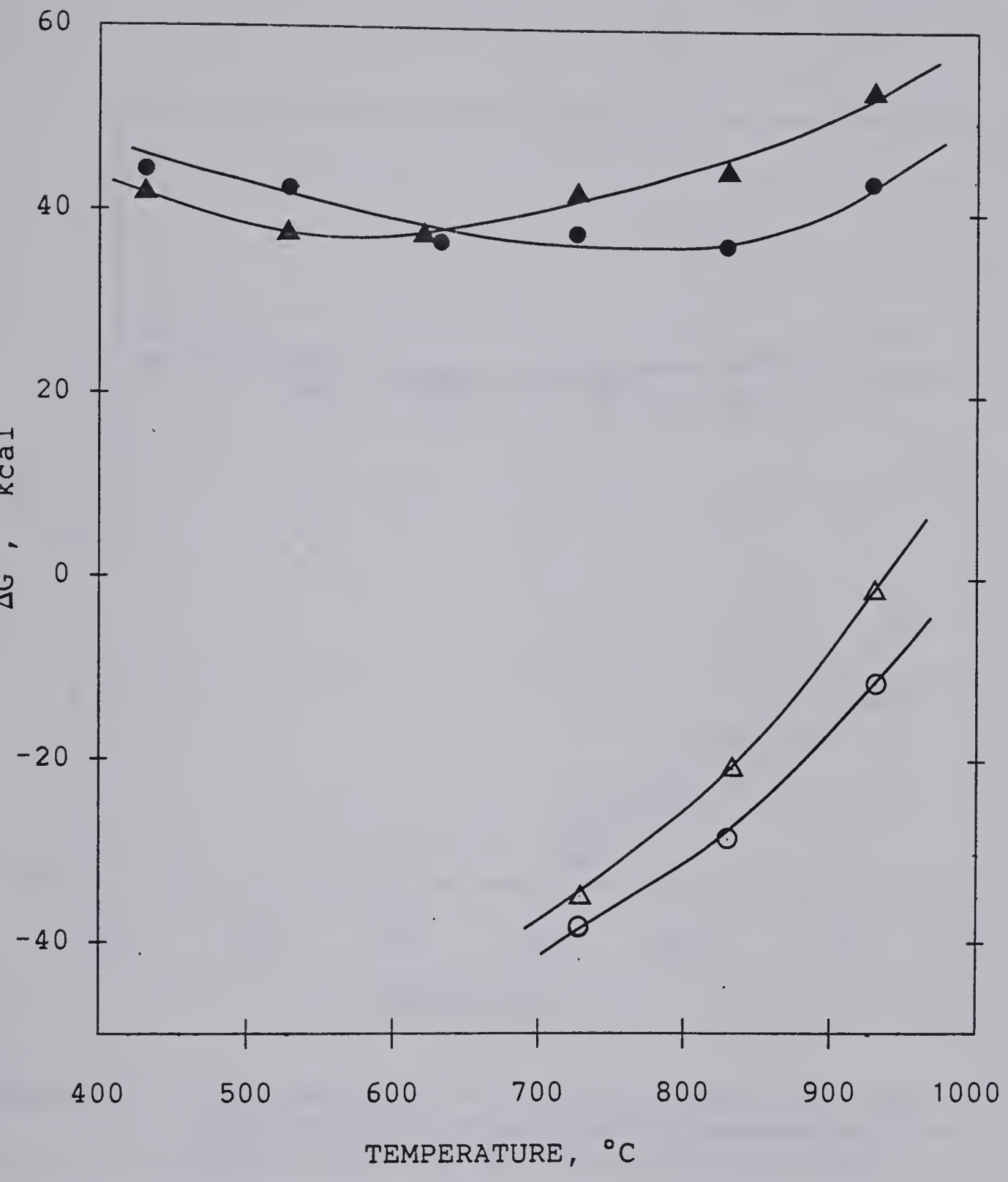

Figure 5. The Standard Free Energy of Reaction for the Formation of Sodium Pyrovanadate from Sodium Chloride and Vanadium Pentoxide.

▲ $4NaCl(l) + V_2O_5(s, l) + O_2 \leftrightarrow Na_4V_2O_7(s) + 2Cl_2$

△ $4NaCl(g) + V_2O_5(s, l) + O_2 \leftrightarrow Na_4V_2O_7(s) + 2Cl_2$

● $4NaCl(l) + V_2O_5(s, l) + 2H_2O \leftrightarrow Na_4V_2O_7(s) + 4HCl$

○ $4NaCl(g) + V_2O_5(s, l) + 2H_2O \leftrightarrow Na_4V_2O_7(s) + 4HCl$

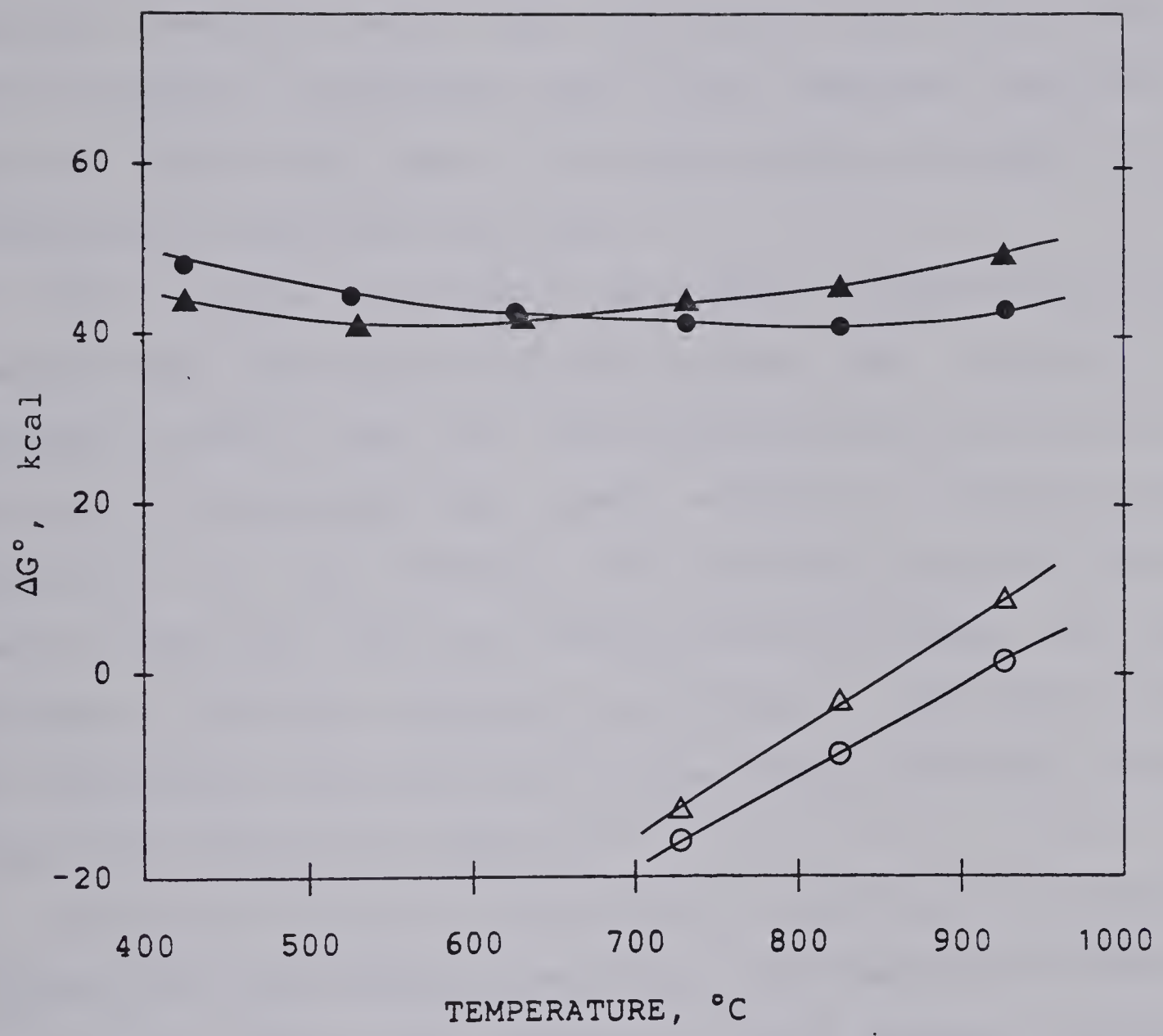

Figure 6. The Standard Free Energy of Reaction for the Formation of Sodium Orthovanadate from Sodium Chloride and Vanadium Pentoxide.

▲ $3NaCl(l) + 1/2\ V_2O_5(s, l) + 3/4\ O_2 \leftrightarrow Na_3VO_4(s) + 3/2\ Cl_2$

△ $3NaCl(g) + 1/2\ V_2O_5(s, l) + 3/4\ O_2 \leftrightarrow Na_3VO_4(s) + 3/2\ Cl_2$

● $3NaCl(l) + 1/2\ V_2O_5(s, l) + 3/2H_2O \leftrightarrow Na_3VO_4(s) + 3HCl$

○ $3NaCl(g) + 1/2\ V_2O_5(s, l) + 3/2H_2O \leftrightarrow Na_3VO_4(s) + 3HCl$

pentoxide has an activity of 1. The reactions involving solid sodium chloride could occur if the chlorine or hydrogen chloride was continuously removed such that the partial pressures were kept well below 1 atm. Also, there may be vanadium compounds other than vanadium pentoxide present which may react with solid sodium chloride in an energetically favorable reaction.

The vanadium extraction decreased slightly when the "carbon-free" ash/sodium chloride mixture was roasted in nitrogen rather than air. This demonstrates that when the fly ash is preroasted, only small amounts of oxygen are required for the moisture free sodium chloride roast reaction (Eq.[2]). The only known sources of oxygen in the nitrogen roasting atmosphere were the air retained in the fly ash bed and the technical nitrogen which contains less than 0.1% oxygen as an impurity.

Decarbonizing the fly ash prior to roasting with sodium chloride was particularly beneficial. This beneficial effect is presumably due to the removal of the unburned carbon rather than chemical changes in the inorganic portion of the fly ash. Little chemical change would be expected at 500°C in view of the temperature at which the fly ash was formed. The effect of carbon was investigated further in the following experiment: samples of "carbon-free" fly ash were mixed with 25% sodium chloride and with 40% of activated charcoal, pulverized Suncor coke, or Syncrude fluid coke, respectively. The mixtures were roasted using the conditions

of Trial 19, and the vanadium extractions by hot-water leaching were 80.3%, 61.9%, and 51.9%, respectively. These results show that a high-surface-area, reactive carbon such as activated charcoal is less detrimental than a slow-burning, more-refractory carbon such as Syncrude coke.

The detrimental effect of carbon could result from the reduction of vanadium to the tetravalent or trivalent oxidation state. The reduced vanadium can react with the alkali to form water-insoluble compounds which are stable when the conditions subsequently become oxidizing. Also, sodium chloride vapor is being carried away during combustion of the carbon and is not available for reaction with pentavalent vanadium when the conditions become oxidizing.

Reduction of vanadium to the tetravalent state by unburned carbon in the fly ash bed is feasible. Vanadium pentoxide is reduced to vanadium tetroxide at 927°C when the oxygen partial pressure drops below 1.39×10^{-3} atm (103). Further reduction to vanadium trioxide (V_2O_3) may be possible but unlikely as the oxygen partial pressure must drop below 8.91×10^{-11} atm (103). The partial pressures of oxygen were calculated using the free energy of reaction data of Mah (103) for the reactions $V_2O_5 \rightarrow V_2O_4 + 1/2\ O_2$ and $V_2O_4 \rightarrow V_2O_3 + 1/2\ O_2$ and the relation $\Delta G^\circ = -RT\ln K$.

The lower valence oxides are reactive with alkali salts. A study of the reactivity of vanadium oxides of various valencies with sodium carbonate showed that the

reactivity increased in the order $V_2O_5 < V_3O_7 < V_6O_{13} < V_2O_4$ (104). The products of the reactions were sodium vanadium "bronzes" of the $Na_2O-V_2O_4-V_2O_5$ ternary system. In the absence of oxygen, "bronzes" also formed in the reaction between V_2O_5 and Na_2CO_3. The "bronzes" of the $Na_2O-V_2O_4-V_2O_5$ system are stable under one atmosphere of oxygen (55). After the carbon has been burned and the conditions become oxidizing, the excess alkali salt which could act to convert these compounds to sodium metavanadate has been lost through volatilization. Vanadium "bronze" chemistry could also explain why the cooling rate affects the vanadium extraction.

G. Optimization of the Sodium Chloride Roast Process

The screening design and follow-up experiments showed that each of the nine factors affected the formation of water-soluble vanadium in the sodium chloride roast process. Since the optimization of a process for nine factors is an unwieldy problem, the following simplifications were made:

1. Undried air was selected as the roast atmosphere since this would be highly preferred industrially. The use of an externally-fired roasting vessel rather than an internally-fired vessel would prevent the introduction of water vapor through fuel combustion;
2. Similarly, the cooling rate of the roast was selected to be a quench. In industrial practice, the roast could pass through a heat exchanger and then be discharged

directly into the leach water;

3. The results with respect to bed depth and gas flow rate indicate that the roasting could be carried out in two stages in a rotary kiln: in the first stage, the fly ash would be decarbonized in excess air at an optimum temperature. In the second stage, the decarbonized fly ash would be roasted with sodium chloride at an optimum temperature and air flow rate. Optimization of flow rate was not considered in this study because of the dependence on the geometry of the roasting system used.

With these considerations the sodium chloride roast process was optimized with respect to decarbonization conditions (temperature), roasting conditions (temperature, time), and the amount of sodium chloride added. The effect of adding sodium chloride to the fly ash "as-received" followed by decarbonization and roasting was also studied.

Because of the large number of samples required for the optimization studies, the roasting was carried out in covered crucibles placed in a muffle furnace. Four to six samples could be run simultaneously. In a test experiment, "carbon-free" fly ash (6 g) containing 25% sodium chloride was roasted at 900°C for 4 hr in crucibles which were immediately withdrawn from the furnace upon completion of roasting. The vanadium extraction was 85%, slightly lower than the extraction obtained in Trial 19.

Optimization of the Roasting Time and the Amount of Sodium Choride

"Carbon-free" fly ash was roasted with 25 percent sodium chloride for various lengths of time. The vanadium extraction reached a maximum of 90% after 4 to 6 hr (Figure 7). The optimum weight ratio of sodium chloride in the "carbon-free" fly ash was 25 percent (Figure 8). These optimum conditions are the same as those determined by Griffin (5).

Excess sodium chloride inteferes with the formation of water-soluble vanadium and two possible explanations were offered by Griffin (5). One is that the liquid sodium chloride forms a barrier which hinders oxygen from reaching the reaction sites. Another is that as the amount of sodium chloride is increased, there is an increased formation of glassy silicate which entraps the vanadium.

Optimization of the Roasting Temperature and the Decarbonization Conditions

Samples of fly ash were decarbonized at temperatures between 500 and 900°C in porcelain crucibles. The time for decarbonization varied from 24 hr at 500°C to 8 hr at 900°C. The "carbon-free" fly ash was mixed with 25% sodium chloride and roasted at temperatures varying between 600 and 1000°C. The results show that the vanadium extraction was a maximum when the decarbonization temperature was 600°C and the roasting temperature was about 840°C (Figures 9 and 10). The roast produced under these conditions contained 2.65% vanadium and the extraction was 85.7%. Increasing the

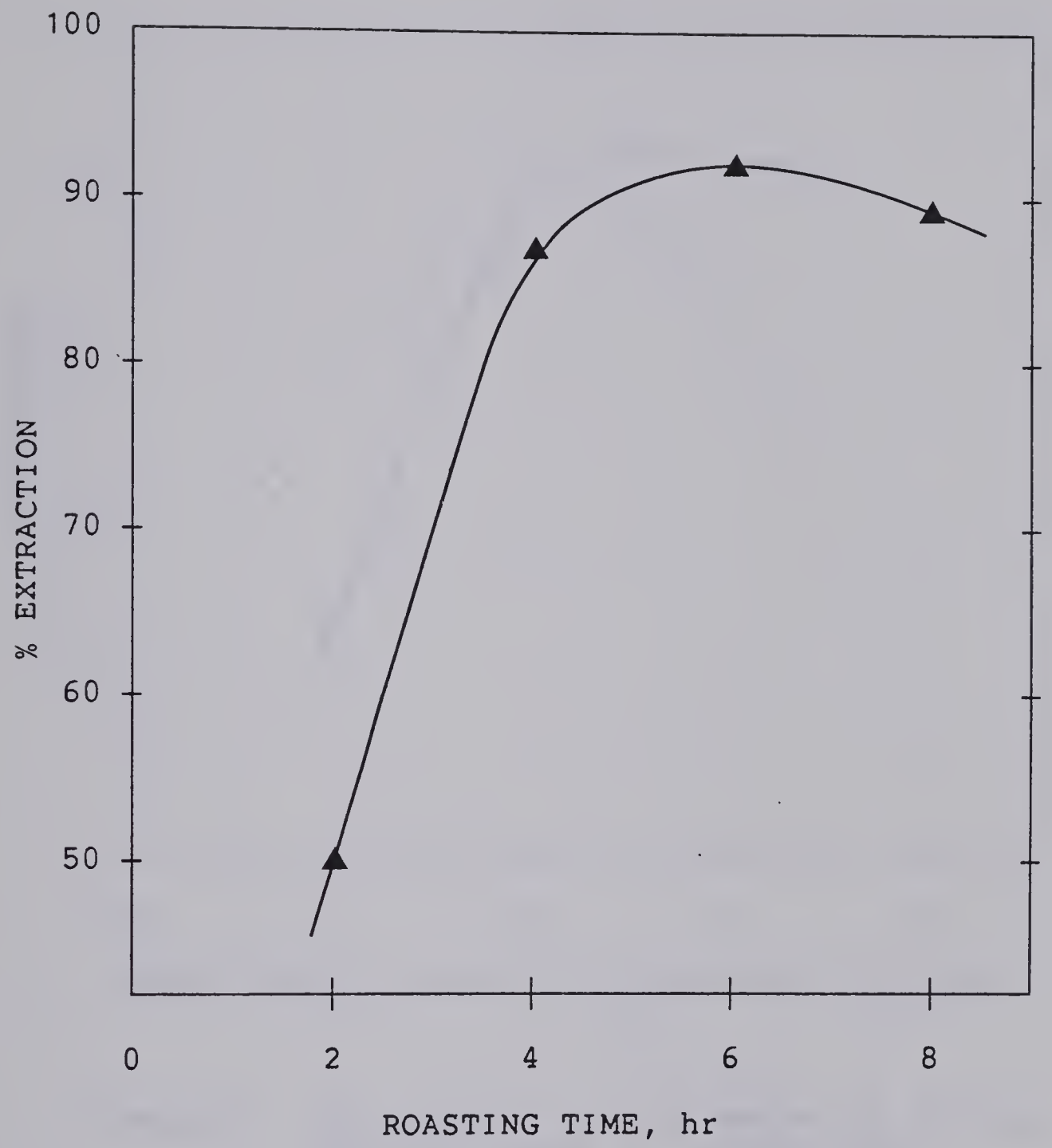

Figure 7. Optimization of Roasting Time.

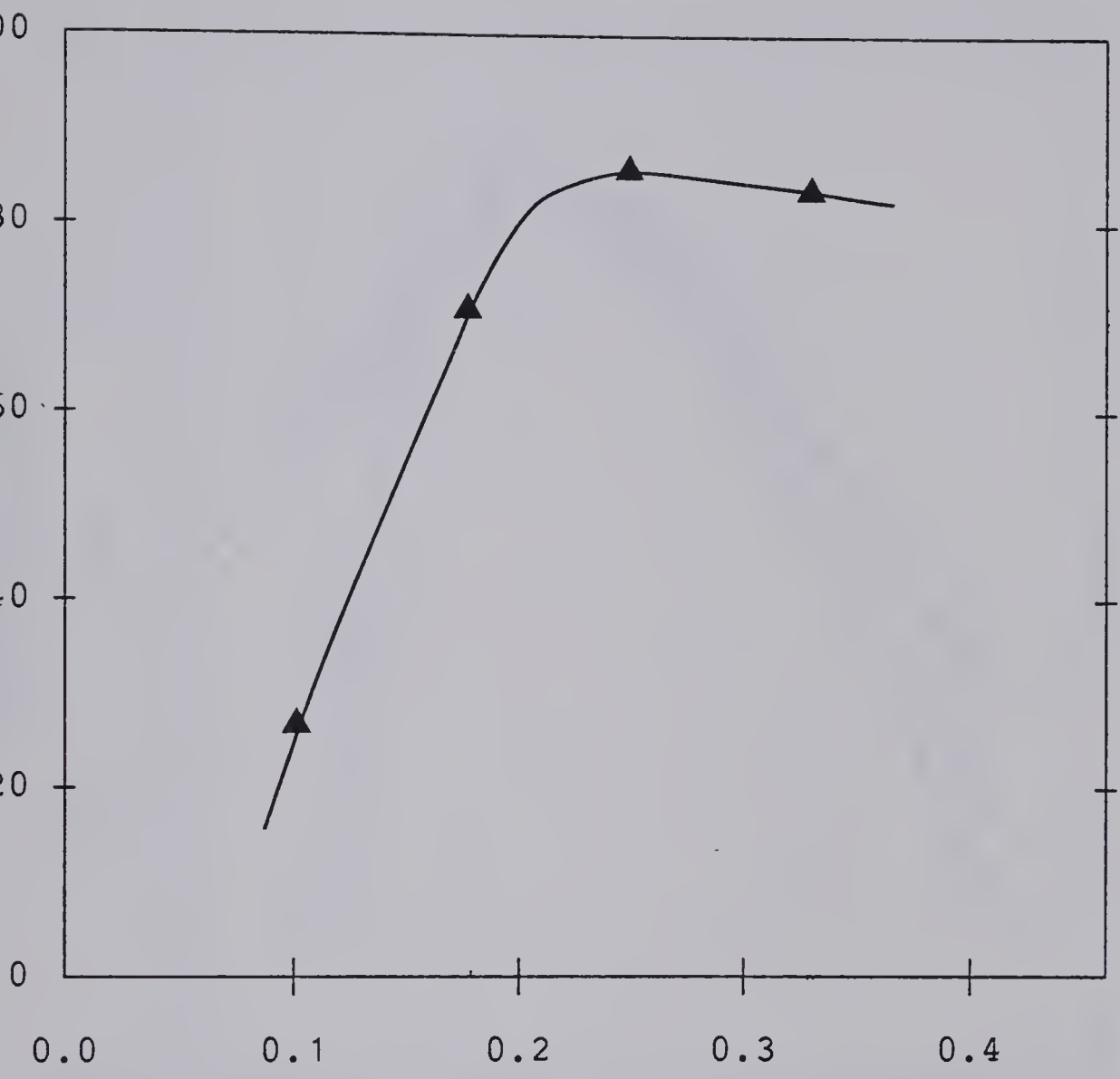

Figure 8. Optimization of the Amount of Sodium Chloride Added to "Carbon-Free" Fly Ash.

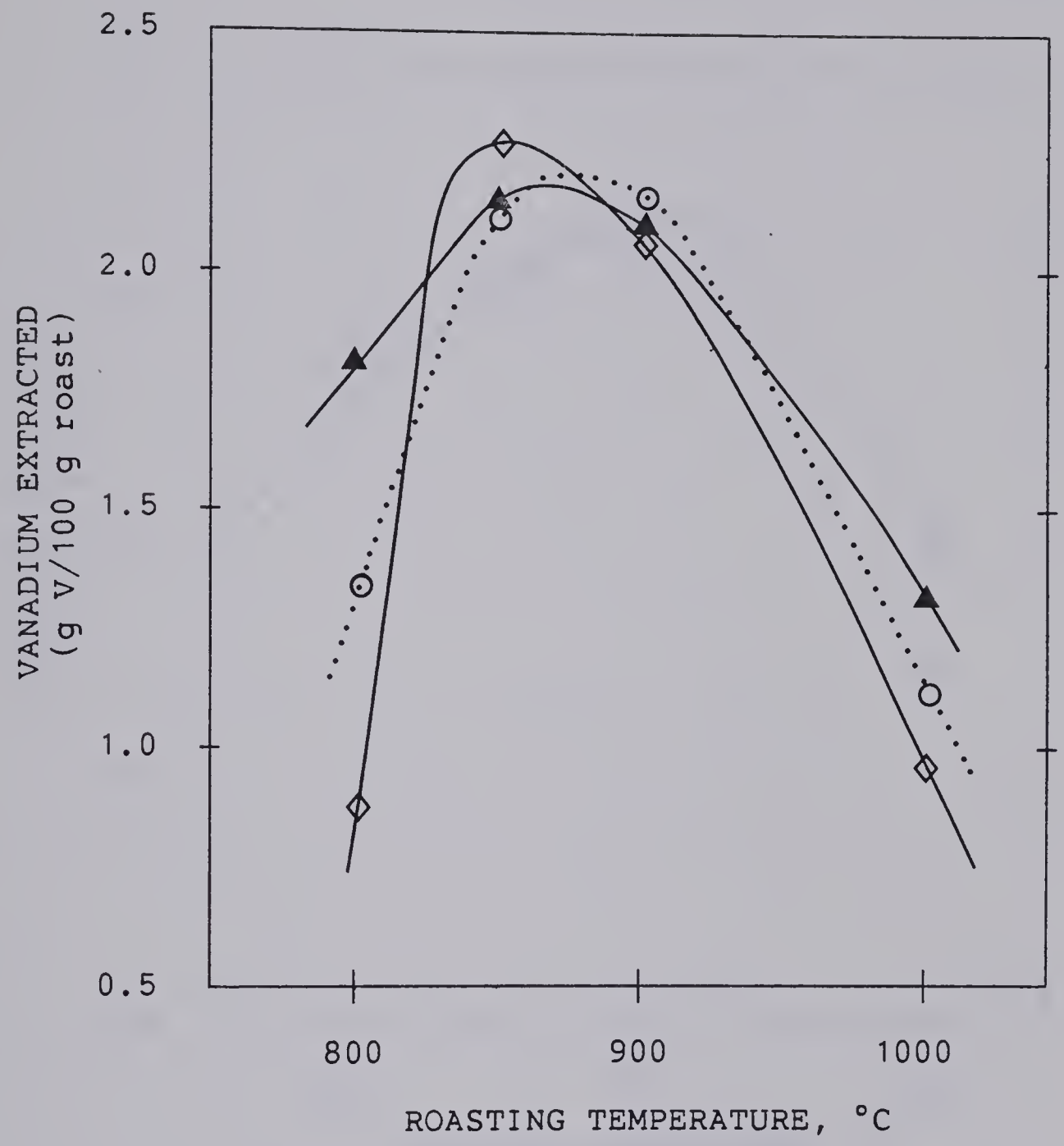

Figure 9. Vanadium Extraction as a Function of Roasting Temperature for Fly Ash Preroasted at 500, 600, and 700°C.
▲ 500, ◇ 600, O 700.

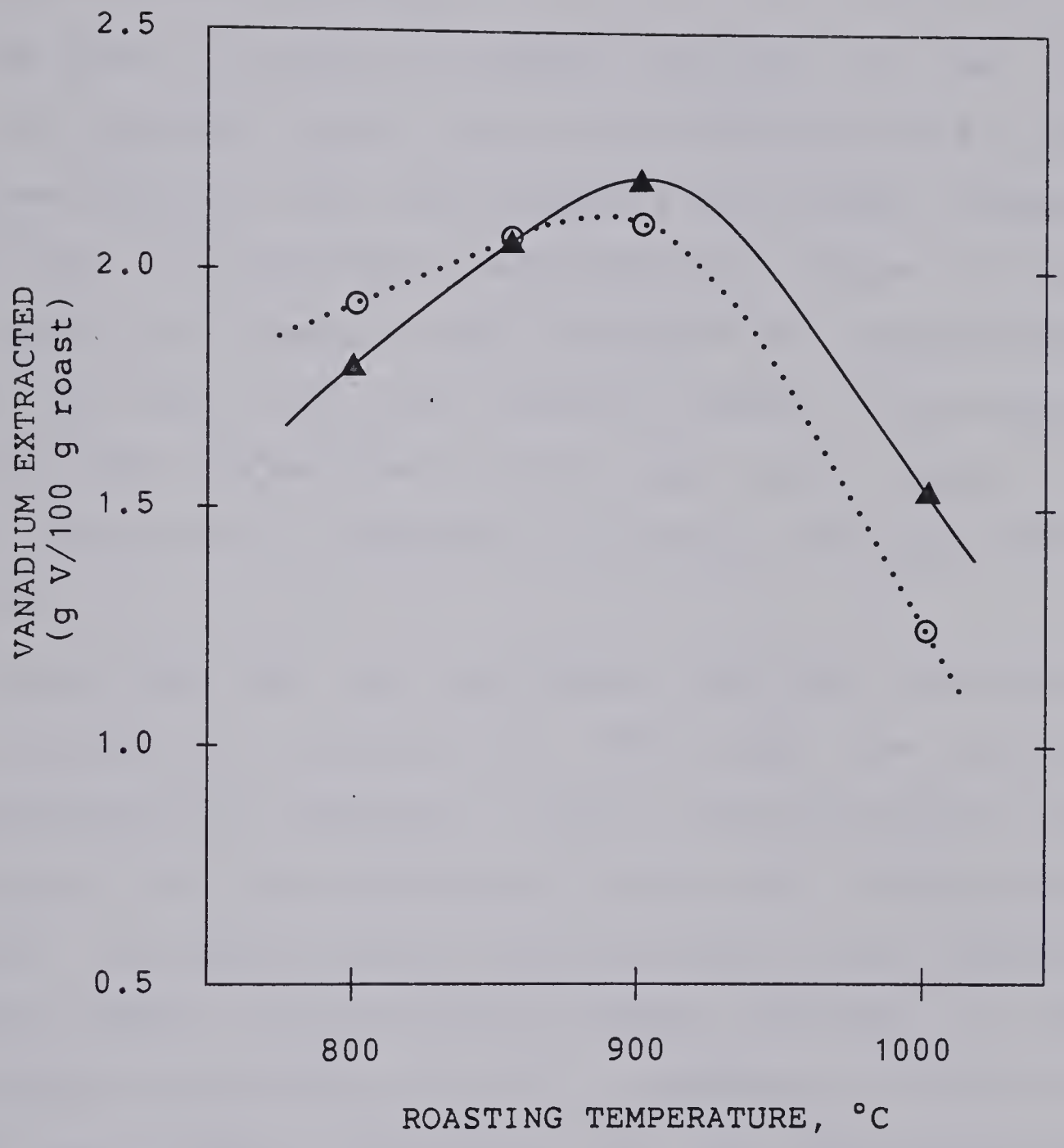

Figure 10. Vanadium Extraction as a Function of Roasting Temperature for Fly Ash Preroasted at 800 and 900°C.
▲ 800, O 900.

decarbonization temperature from 500°C to 900°C shifted the optimum roasting temperature from 840°C to 900°C. The roasts produced at the optimum for each decarbonization temperature contained 2.6 ±0.1% vanadium.

The effect of adding the sodium chloride to the fly ash, "as-received," rather than to the decarbonized fly ash was investigated as this would simplify the process. Samples of fly ash "as-received" were mixed with sodium chloride (25% "carbon-free" basis) and preroasted at temperatures between 500 and 800°C to constant weight in porcelain crucibles. The "carbon-free" solids were then roasted in covered crucibles at temperatures between 700°C and 1000°C for 4 hr.

Preroasting the fly ash/sodium chloride mixture at 500°C followed by roasting at 900°C gave the optimum vanadium extraction (Figures 11 and 12). This extraction was the same as that obtained when the fly ash was decarbonized at 500°C followed by sodium chloride addition and roasting at 840°C. However, the presence of sodium chloride in the fly ash during decarbonization at a temperature of 600°C or greater was highly detrimental. As the decarbonization temperature was increased from 500°C to 700°C, the optimum roasting temperature dropped from 900 to 800°C and the optimum vanadium extraction dropped by 25%. At 800°C, the optimum roasting temperature increased to 850°C. This anomaly could occur because sodium chloride melts at 801°C.

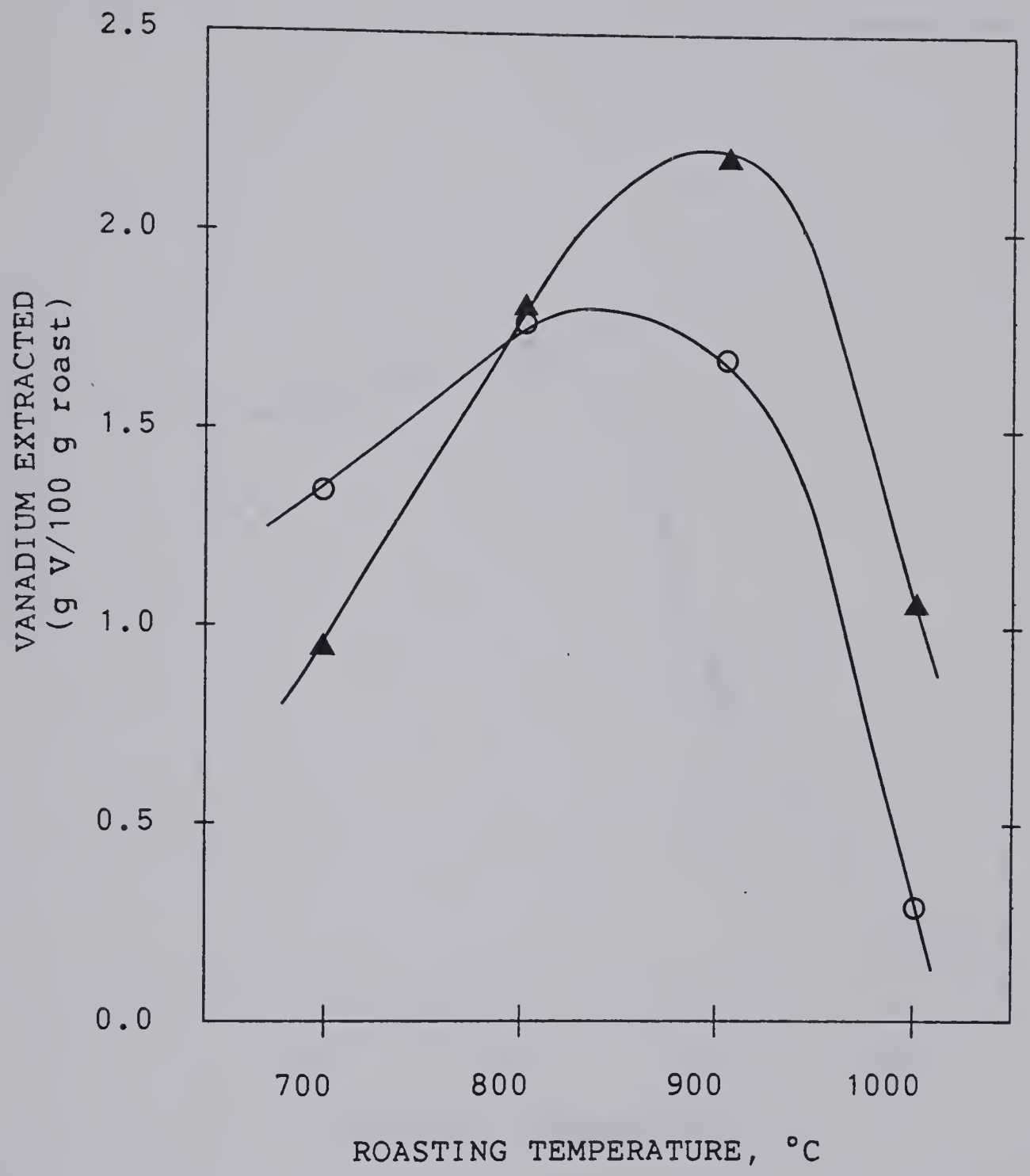

Figure 11. Vanadium Extraction as a Function of Roasting Temperature When Sodium Chloride is Added to Fly Ash Prior to Preroasting at 500 and 600°C.
▲ 500, O 600.

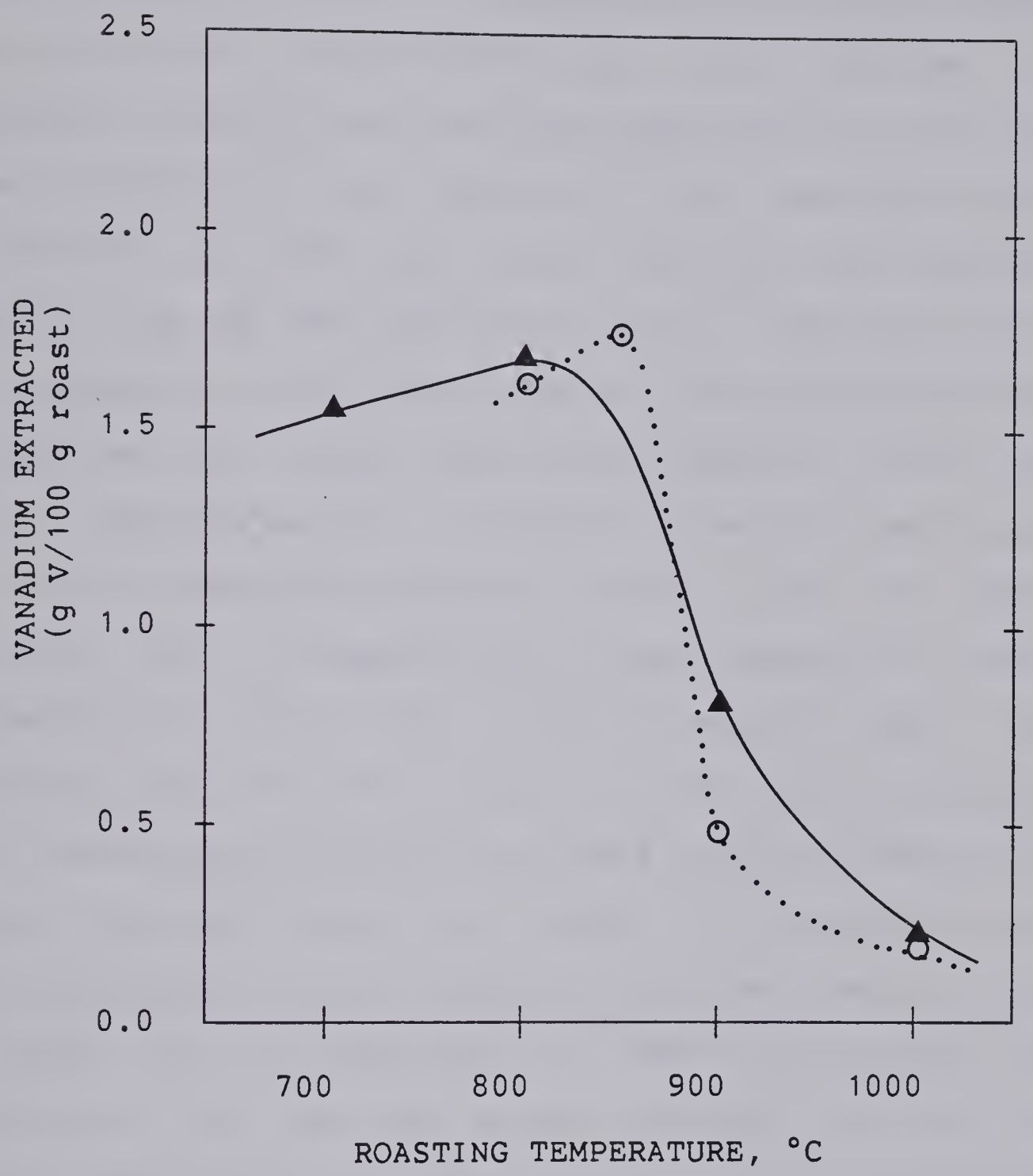

Figure 12. Vanadium Extraction As a Function of Roasting Temperature When Sodium Chloride is Added to Fly Ash Prior to Preroasting at 700 and 800°C.
▲ 700, O 800.

Several additional experiments were done to determine if the detrimental effect was due to reactivity at low temperatures between sodium chloride and the aluminosilicate in the fly ash. "Carbon-free" fly ash obtained by preroasting at 600°C was mixed with 25% sodium chloride and roasted at 600°C for 4 hr. Samples of the resulting solid were roasted at 800°C and 900°C for 4 hr. The vanadium extraction from the 800° roast was 1.87 g vanadium/100 g roast compared to the extraction of 1.78 g vanadium/100 g roast obtained when sodium chloride was added to the fly ash prior to decarbonization at 600°C followed by roasting at 800°C. The corresponding vanadium recovery from the 900°C roast was 1.96 g vanadium/100 g roast compared to 1.65 g vanadium/100 g roast. The results indicate that the detrimental reactions still occured at 600°C but to a lesser extent. The detrimental reactions could involve formation of vanadium "bronzes" which are stable in air and are not easily converted to sodium vanadate (55). The results also show that it is desirable to heat the mixture of "carbon-free" fly ash and sodium chloride rapidly to roasting temperature in order to avoid the detrimental reactions.

H. Precipitation of Ammonium Metavanadate and Red Cake from the Leachate

Because the leachate contained primarily sodium vanadate with sodium sulfate as the only impurity present in appreciable concentration, recovery of vanadium from the

leachate by direct precipitation of ammonium metavanadate or red cake was investigated.

Experimental

To produce the large volumes of ash required for the leaching experiments, 75 g batches of fly ash decarbonized at 600°C were roasted in a 250 ml zirconia crucible. The optimum conditions determined above were used: 25% sodium chloride, 850°C, 4 hr. The vanadium extraction from the solid was 77%. The reduction was attributed to insufficient gas flow due to the increased bed depth, 6 cm, compared to 2 cm in the crucible and boat tests.

The leachate was prepared for the precipitation studies by leaching the pulverized roast with hot water (100 g ash/100 g water) at 95°C for 1 hr in an Erlenmeyer flask. The leachate was filtered from the solid using a Buchner funnel and 20 ml aliquots were taken for the precipitation studies. The leachate was kept hot (80 to 90°C) prior to use to avoid the slight precipitation which occured when the leachate cooled.

Ammonium metavanadate was precipitated from the leachate by addition of ammonium chloride crystals. The reagent was added in crystalline form rather than as a solution to avoid dilution of the leachate. Red cake was precipitated from the leachate by addition of 2M sulfuric acid. The precipitations were carried out in 50 ml glass beakers. The precipitate was collected in preweighed Gooch

crucibles which had previously been dried at 100°C with glass-fiber filters in place. The crucibles with the filtered precipitates were dried at 100°C overnight and the weight of the precipitate determined by difference. The elemental composition of the precipitate was determined by dissolving 0.1 g in 10 ml of water/5 ml concentrated hydrochloric acid and analyzing the resulting solution by ICP. Samples of the starting leachate and filtrates were also analyzed by ICP. Of the vanadium originally present in the leachate, 102 ±2% was accounted for in material balance calculations.

Precipitation of Ammonium Metavanadate

The starting leachate had a pH of 5.5-6.0 and was an intense orange color, characteristic of the decavanadate ions ($HV_{10}O_{28}^{-5}$ or $H_2V_{10}O_{28}^{-4}$) which are the dominant species at this pH and vanadium concentration. The leachate contained 32.3 g/l vanadium pentoxide equivalent, 27.0 g/l sodium, and low concentrations of other elements (Table 10).

The precipitation of ammonium metavanadate was studied as a function of pH and ammonium chloride concentration. Two ammonium chloride concentrations were used: 0.80M and 1.40M which correspond to mole ratios in the leachate of 2.24 and 4.40 NH_4Cl:V, respectively.

The precipitation at a pH of 5.5 was studied by adding ammonium chloride directly to a 20 ml aliquot of hot leachate (85°C). The ammonium chloride dissolved quickly to

Table 10. Analysis of the Leachate Used for the Precipitation Experiments

ELEMENT	CONCENTRATION (g/l)
Ca	0.63
Na	27.0
Ni	0.07
Fe	0.02
Al	0.04
V_2O_5	32.3
S	3.8
Si	0.12

give a precipitate free solution. Upon cooling to room temperature a yellow precipitate formed. After 4 hr, it was collected, washed with 10% ammonium chloride solution, and dried overnight at 100°C. The analysis showed that only 40% of the vanadium had precipitated, and that the solid contained 4.5% sodium (Table 11). It was concluded that a high purity product cannot be obtained by direct addition of ammonium chloride to the leachate. X-ray diffraction analysis produced a powder pattern with many high angle peaks. However, no compounds could be identified.

To study the ammonium metavanadate precipitation at pH 7, 9, and 11, a solution of 1M NaOH/1M Na_2CO_3 was added to 20 ml aliquots of the leachate prior to addition of the ammonium chloride. A solution containing carbonate was used to avoid the precipitation of calcium vanadate as the pH was raised since calcium carbonate precipitates in preference to calcium vanadate (24, 105).

Addition of the alkali caused the precipitation of a green-grey sludge which was difficult to filter when initially formed. Digestion for 0.5 hr at 90 to 95°C converted the precipitate into a solid that could be readily filtered. The filtered solution was colorless, indicating that the predominant species in solution was no longer the decavanadate but metavanadate or pyrovanadate. Analysis of the sludge showed that 4.2%, 5.4%, and 3.7% of the vanadium precipitated during the pH adjustment to 7, 9, and 11, respectively. At pH 7, 10.2% of the calcium, 100% of the

Table 11. Precipitation of Ammonium Metavanadate from the Leachate

pH of LEACHATE	MOLE RATIO' NH_4Cl:V	VOLUME(ml) 1M Na_2CO_3/ 1M NaOH	% VANADIUM PRECIPITATED	ANALYSIS OF PRODUCT, WT%							
				V_2O_5	Na	Ca	S	Si	Al	Ni	Fe
5.5	2.24	0.0	39.7	83.4	4.47	0.16	0.09	0.06	0.17	0.03	0.06
7.0	2.24	0.7	54.1	76.7	0.10	0.02	0.05	0.20	<0.03	<0.01	0.02
	4.30	0.5	70.0	77.3	0.27	0.02	0.05	0.17	<0.03	<0.01	0.02
9.0	2.24	2.0	67.0	77.2	0.22	0.02	0.05	0.08	<0.03	<0.01	0.01
	4.38	1.6	86.2	76.2	0.24	0.02	0.05	0.08	<0.03	<0.01	0.02
11.0	2.44	2.2	72.6	77.9	0.10	<0.01	<0.02	<0.07	<0.03	<0.01	<0.01
	4.30	2.2	102.0	78.4	0.09	<0.01	<0.02	<0.06	<0.03	<0.01	<0.01

'The corresponding concentrations of ammonium chloride in solution are 0.80M (2.24 NH_4Cl:V) and 1.40M (4.30 NH_4Cl:V)

nickel, 68.5% of the iron, 70% of the aluminum and 20% of the silicon had precipitated. As the pH was increased, the extent of precipitation increased, and at pH 11 approximately 100% of the calcium, nickel, iron, aluminum, and silicon had precipitated. Sulfate stayed in solution throughout the pH range of 5.5 to 11. These results indicate that the addition of concentrated ammonia to precipitate ammonium metavanadate is not feasible as the ammonium metavanadate would be contaminated by the sludge that precipitates as the pH is raised.

After removal of the sludge from the pH adjusted leachate, the solution was cooled to room temperature, and the ammonium chloride crystals added. The crystals dissolved rapidly and precipitation of ammonium metavanadate started almost immediately. The precipitate was digested for 0.5 hr at room temperature during which the initial fine particulate developed into large filterable crystals. The white crystals were collected, washed with four 2-ml volumes of 10% ammonium chloride solution and dried overnight at 100°C.

Table 11 contains the details of the precipitation procedure and the analysis of the ammonium metavanadate product. The extent of vanadium precipitation from the leachate increased as the pH was increased, and as the concentration of ammonium chloride increased. The highest precipitations were obtained at pH 9 (86%) and pH 11 (≃100%) with the mole ratio of NH_4Cl:V = 4.30. The precipitate

formed at pH 7, 9, and 11 was ammonium metavanadate as confirmed by X-ray diffraction analysis and chemical analysis. The various solids contained between 76.7 and 78.4% V_2O_5 equivalent, comparable to the theoretical concentration of 77.4% V_2O_5 equivalent in pure ammonium metavanadate. The purity of the ammonium metavanadate, particularly with respect to sodium, increased as the pH was raised from 5.5 to 11. At pH 11, the product contained 0.10% sodium as the major impurity. Qualitative elemental analysis by X-ray fluorescence indicated that a low concentration of chloride was also present, likely as sodium or ammonium chloride.

Precipitation of Red Cake

The pH of 20 ml aliquots of hot leachate was decreased to either 2.0 or 1.5 by addition of 2M sulfuric acid. Large red shot-like particles began to precipitate immediately. The precipitation was continued for 0.5 hr at 85 to 90°C. The crystals were filtered from the aqueous solution without washing and dried at 100°C.

The details of the precipitation, the yield, and the elemental analysis is shown in Table 12. Precipitation of red cake containing 91.5% V_2O_5 equivalent was quantitative at a pH of 1.5. At either pH, the red cake contained appreciable sodium (3 to 4%) but concentrations of 0.1% or less of other impurities such as calcium, silicon, aluminum, nickel, and iron. Analysis of the red cake by X-ray

Table 12. Precipitation of Red Cake from the Leachate

	LEACHATE pH	
	1.5	2.0
VOLUME 2M H_2SO_4 (ml)	1.6	1.0
% VANADIUM PRECIPITATED	101.0	46.0
ANALYSIS OF PRODUCT(%):		
V_2O_5	91.5	85.3
Na	3.01	4.15
Ca	0.01	0.12
S	0.08	0.42
Si	0.07	0.10
Al	0.05	0.07
Ni	<0.01	0.01
Fe	0.06	0.09

diffraction produced a pattern containing three, broad, low-intensity peaks, which indicated that the precipitate was amorphous.

I. Conclusions

This study shows that vanadium can be extracted from Suncor fly ash by the sodium chloride roast/hot-water leach process and that factors in addition to those studied by Griffin (5) affect the extent to which water-soluble vanadium compounds form. Unburned carbon, high moisture levels, and either excessive or inadequate gas/solid interaction during the roasting were highly detrimental. The reasons for the decreased vanadium extraction could only be postulated, however. High purity ammonium metavandate was precipitated from the leachate but a pH adjustment and filtration due to the accompanying precipitation of impurities was required. Solvent extraction could be investigated as an alternative technique for the conversion of vanadium in the leachate to ammonium metavanadate. Recovery of vanadium from the leachate by precipitation of red cake is also feasible, but purification of the red cake would be required if high purity vanadium pentoxide is required as a final product.

IV. EXTRACTION OF VANADIUM AND NICKEL FROM THE ASH OF LOW-SULFUR-EMISSION COKE

The recovery of vanadium (and nickel) from the ash of low-sulfur-emission coke appeared to be much simpler than from Suncor fly ash. As a consequence of adding the calcium hydroxide reagent to the bitumen, the resulting coke ash contained acid-soluble vanadium and nickel which can be leached directly without further treatment as shown by Schneider and George (6). The objective in this study was to determine how the vanadium and nickel in the leachate could be converted to saleable end products.

A. Experimental

Laboratory coke was generated using the method of George, Schneider, and Kessick (48). Athabasca bitumen containing 4.8% calcium hydroxide was coked at 480°C for 2 hr. Each run generated 8.3 g of coke. The coke was pulverized with a mortar and pestle and ashed to constant weight in ceramic crucibles which were placed directly into a muffle furnace preheated to 900° C. The ashing took 18 to 20 hr. The coke yielded 47% ash, reflecting the large amount of sulfur retained in the ash as calcium sulfate (6). The elemental composition of the ash was determined by the lithium metaborate fusion method described in Chapter III.

The ash was leached for 1 hr at 95°C in the leachate of choice (2M hydrochloric acid, 2M sulfuric acid, or 2M sodium carbonate). The leachate was analyzed by ICP and the metal extraction reported as percent extraction.

B. Analysis of Ash

The analysis of the ash is shown in Table 13. The vanadium and nickel concentrations are low compared to that in Suncor fly ash because of the large amount of sulfur retained in the ash as calcium sulfate. The calcium oxide and calcium sulfate concentrations shown in Table 13 were calculated on the basis of the calcium and sulfur analysis of the ash. Calcium sulfate and calcium oxide were identified by X-ray diffraction analysis (powder method) of the ash. All of the peaks present in the pattern corresponded to either calcium sulfate or calcium oxide.

C. Recovery of Vanadium from the Acid Leachates

The analysis of the leachate obtained by leaching 2.4 g ash with 50 ml of 2M hydrochloric acid is shown in Table 14. The vanadium and nickel extraction was 99% and 82%, respectively, in agreement with the results reported by Schneider and George (6). The leachate contained 0.20 g/l vanadium pentoxide equivalent and 0.039 g/l nickel.

Solvent extraction is the only method available for recovery of vanadium from leachates containing very low concentrations of vanadium. However, since the vanadium pentoxide concentration in the leachate was below the lower limit for efficient solvent extraction (1 to 2 g/l vanadium pentoxide equivalent), various methods for increasing the vanadium concentration in the leachate were investigated, as well as solvent extraction of vanadium from the leachate.

Table 13. Analysis of the Ash from Low-Sulfur-Emission Laboratory Coke

ELEMENT	CONCENTRATION (%)
V	0.23
Ni	0.09
Fe	0.60
Si	1.7
Al	1.2
Ca	31.6
S	17.2
CaO	14.2
$CaSO_4$	73.2

Table 14. Analysis of the Hydrochloric Acid Leachate

ELEMENT	g/l	% EXTRACTED
V (V_2O_5)	0.11 (0.20)	99
Ni	0.039	82
Fe	0.18	63
Ca	9.3	61
S	6.3	76
Si	0.50	62
Al	0.65	97

Although nickel recovery from the leachate was not included in this study, the nickel could possibly be recovered by precipitation of nickel oxide through pH adjustment or precipitation of nickel sulfide by hydrogen sulfide.

The concentration of vanadium in the leachate could theoretically be increased by increasing the pulping ratio (g ash/ml leachate) and by leaching several batches of ash with a single batch of leachate. To investigate this possibility, three batches of ash were leached with one batch of 2M hydrochloric acid. The pulping ratio in each batch varied from 0.074 to 0.10. The concentrations of vanadium, nickel, and calcium in the leachate and the cumulative recoveries after each batch are shown in Table 15. The first two batches were extracted satisfactorily with only a slight reduction in cumulative nickel recovery. However, during the extraction of the third batch copious precipitation occurred, the pH of the leachate increased to 6, and the vanadium and nickel concentration in the leachate dropped to less than 0.01 g/l. Further analysis of the leachate showed that it contained a high concentration of calcium chloride and a low concentration of sulfate.

The best explanation for these results is that the calcium oxide in the ash neutralized the hydrochloric acid leachate causing precipitation of the acid-soluble calcium sulfate and calcium vanadate. Nickel could be removed from the leachate through adsorption or occlusion in the calcium sulfate precipitate since precipitation of nickel hydroxide

Table 15. Leaching Multiple Batches of Ash With 2M Hydrochloric Acid

BATCH	PULPING RATIO	CONCENTRATION IN LEACHATE (g/l)			% CUMULATIVE RECOVERY	
		V_2O_5	Ni	Ca	V_2O_5	Ni
1	0.074	0.45	0.055	8.2	99	74
2	0.083	0.96	0.11	16.0	99	66
3	0.10	0.006	0.003	34.4	<0.1	<0.1

would not be expected on the basis of solubility (53).

The amount of hydrochloric acid consumed by the calcium oxide and other basic compounds in the fly ash was determined by the following procedure: a weighed sample of ash was combined with a known volume of 0.2M hydrochloric acid and the slurry digested at room temperature for 8 hr. The remaining acid in the slurry was titrated with standardized sodium hydroxide to a pH of 7. The acid consumption was 2.8 l 2M hydrochloric acid per kilogram of ash (5.6 moles of hydrochloric acid per kilogram ash). This high consumption of acid could make the process economically less feasible. In an industrial scale process, the amount of calcium oxide in the ash might be lower than in the laboratory generated ash. Depending upon combustor conditions, the extent to which calcium hydroxide reacts with the sulfur in the coke to form calcium sulfate may be higher; also, the calcium oxide which forms may scavenge sulfur dioxide and sulfur trioxide in the combustor exit where the lower temperatures favor sulfation. A water leach to remove the calcium oxide and calcium sulfate is not possible because of the low water solubility of these compounds.

In spite of the high acid consumption, the study was continued with the objective of determining a method to recover the vanadium from the ash. Sulfuric acid was used in preference to hydrochloric acid because it is cheaper, less corrosive, and the interference of negatively-charged ferric

chloride complexes with negatively-charged polyvanadate ions during solvent extraction can be avoided. Schneider and George (6) observed that the vanadium extraction by the two leachates was the same but that the nickel extraction was somewhat higher in hydrochloric acid (80% versus 74%). However, the other benefits of sulfuric acid were considered to outweigh the reduction in nickel extraction, and sulfuric acid was used in subsequent acid leach experiments.

As the first step in increasing the concentration of vanadium in the leachate, the pulping ratio was optimized. Samples of ash were leached with 2M sulfuric acid using pulping ratios varying from 0.1 to 0.5. The optimum pulping ratio was 0.40 with 96% of the vanadium and 68% of the nickel extracted (Figure 13). This slurry was very thick, however, so a pulping ratio of 0.3 was selected instead. An analysis of the leachate obtained at a pulping ratio of 0.3 is shown in Table 16. The decrease in vanadium and nickel extraction at a pulping ratio of 0.5 was accompanied by neutralization of the leachate.

To raise the vanadium concentration of the leachate further, the feasibility of leaching several batches of ash with one batch of 2M sulfuric acid leachate was investigated. The pulping ratio was set at 0.30 and concentrated sulfuric acid (18M) was added to the leachate after each batch of ash to make up for the acid neutralized by the ash (1.0 ml acid per 4.0 g ash). The first batch of ash (4.5 g) was leached with 15 ml of 2M sulfuric acid in a

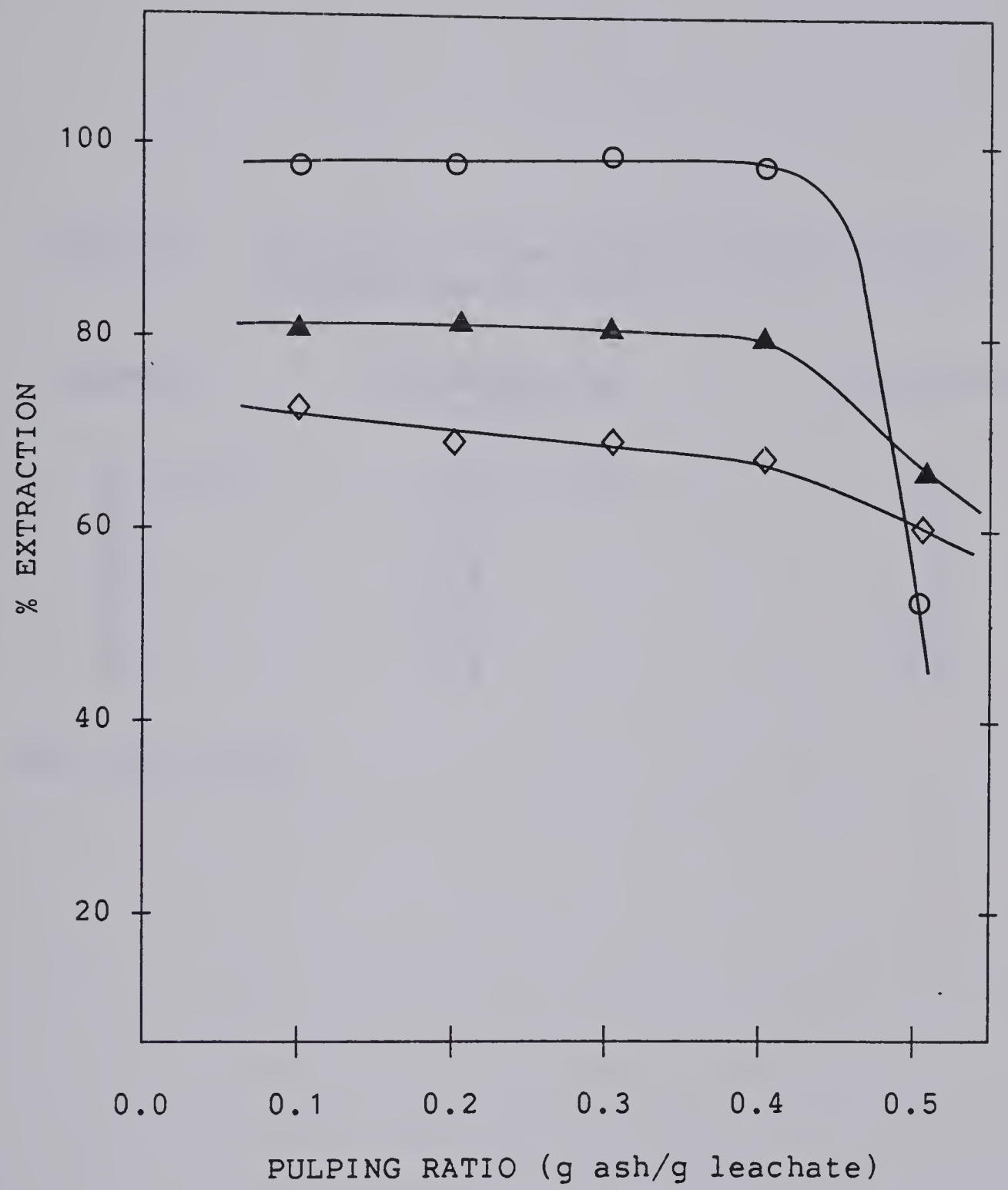

Figure 13. Extraction as a Function of Pulping Ratio in the Extraction of Laboratory Coke Ash With Sulfuric Acid.
○ vanadium, ▲ iron, ◇ nickel.

Table 16. Analysis of the Sulfuric Acid Leachate (pulping ratio = 0.3)

ELEMENT	CONCENTRATION (g/l)	% EXTRACTED
V (V_2O_5)	0.71 (1.27)	99
Ni	0.19	70
Fe	1.4	78
Ca	5.8	6
S	39.5	N/A[1]
Al	3.8	100
Si	3.4	67

[1]Not applicable.

polyethylene bottle which was loosely capped to minimize evaporation of the leachate. The solid was filtered from the leachate, without washing; 1 ml of concentrated sulfuric acid added to the 8.9 ml of leachate collected; and another batch of ash leached. During the leaching of the second batch the slurry gelled, possibly because of silica precipitation, making filtering impossible. Because of this gelling, the vanadium concentration could not be increased by leaching multiple batches of ash. The concentration after leaching one batch of ash in sulfuric acid was 1.3 g/l vanadium pentoxide equivalent. Therefore, the pulping ratio was increased to 0.40 and solvent extraction of the vanadium from the leachate investigated.

The solvent most commonly used for the extraction of pentavalent vanadium is Aliquat 336. The pH of acid leachates must be adjusted to approximately 2 to convert the positively-charged vanadyl ion (VO_3^+) to the negatively-charged polyvanadates which are extracted by the solvent. A sample of the ash was leached with 2M sulfuric acid and the leachate filtered without washing the filter cake. As 5M sodium hydroxide solution was added to the leachate to raise the pH to 2, a gelatinous precipitate formed. Upon stirring and heating (85°C) the gel appeared to break to form a reddish solid. The solid could not be filtered from the solution. Addition of a less concentrated base (2M sodium hydroxide solution) did not change the filterability, and neither did addition of the base to hot

leachate followed by digestion at 85°C for 8 hr. Addition of ammonia or sodium carbonate similarly did not improve the filterability of the precipitate. The analysis of the small amount of leachate that could be filtered before the filter became clogged is shown in Table 17. Forty percent of the vanadium precipitated and the concentrations of the other analyzed elements also decreased by 20 to 40%. Precipitation of iron hydroxide and silica could explain the formation of the gelatinous precipitate.

The conclusions from these experiments are:

1. The vanadium can be extracted from the ash by acid leachates but large amounts of the acid are consumed through reaction with the calcium oxide in the ash;
2. Solvent extraction (Aliquat 336), necessary to concentrate and purify the vanadium, could not be used because the required pH adjustment caused almost half of the vanadium to precipitate as part of a gelatinous precipitate which could not be filtered from the leachate;
3. The recovery of vanadium from the ash by acid leaching and solvent extraction does not appear feasible unless a way to avoid or handle the pH adjustment problem can be found.

Table 17. The Change in Composition of the Leachate After Adjustment of the pH to 2.0

ELEMENT	STARTING LEACHATE (g/l)	pH ADJUSTED LEACHATE (g/l)	PERCENT PRECIPITATION
V (V_2O_5)	1.05 (1.83)	0.64 (1.14)	39
Ni	0.23	0.16	30
Fe	2.0	1.28	36
Ca	1.3	0.86	31
S	28.3	22.7	20
Al	5.0	4.4	23
Si	4.7	3.3	30

D. Recovery of Vanadium with Sodium Carbonate Leachate

Since the recovery of vanadium from an acidic leachate did not appear possible, the use of an alkaline reagent was investigated. Schneider and George (106) observed that 90% of the vanadium in the ash could be extracted by 2M sodium carbonate but that only negligible amounts of vanadium were extracted by 2M sodium hydroxide or 2M ammonium hydroxide. Vanadium has also been extracted from fly ash (107) and from uranium ores (108) by leaching with sodium carbonate. Sodium carbonate is a more expensive reagent than sulfuric or hydrochloric acid and nickel is not extracted (106). However, the concentration of impurities in the leachate would be minimal due to the insolubility of most metal oxides in alkaline solution.

A 0.23 g sample of ash was leached with 5 ml of 2M sodium carbonate for 1 hr at 97° C. The analysis of the leachate showed that the vanadium extraction was 88% (Table 18). Appreciable amounts of silica and alumina, and all of the sulfur in the ash dissolved in the leachate.

The pulping ratio was optimized using the same procedure described for the sulfuric acid leach experiments. Samples of ash were leached with 2M sodium carbonate at pulping ratios of 0.1 to 0.5. The vanadium extraction decreased as the pulping ratio increased and the sulfate in the ash dissolved in the leachate (Figure 14). Calcium carbonate was identified as the only component in the leached solid by X-ray diffraction analysis. In this system

Table 18. Analysis of the Sodium Carbonate Leachate

ELEMENT	CONCENTRATION (g/l)	% EXTRACTED
V (V_2O_5)	0.095 (0.17)	88
Ni	ND[1]	ND
Fe	0.01	3
Ca	0.02	0.1
S	8.5	100
Si	0.33	38
Al	0.16	25

[1]Not detected.

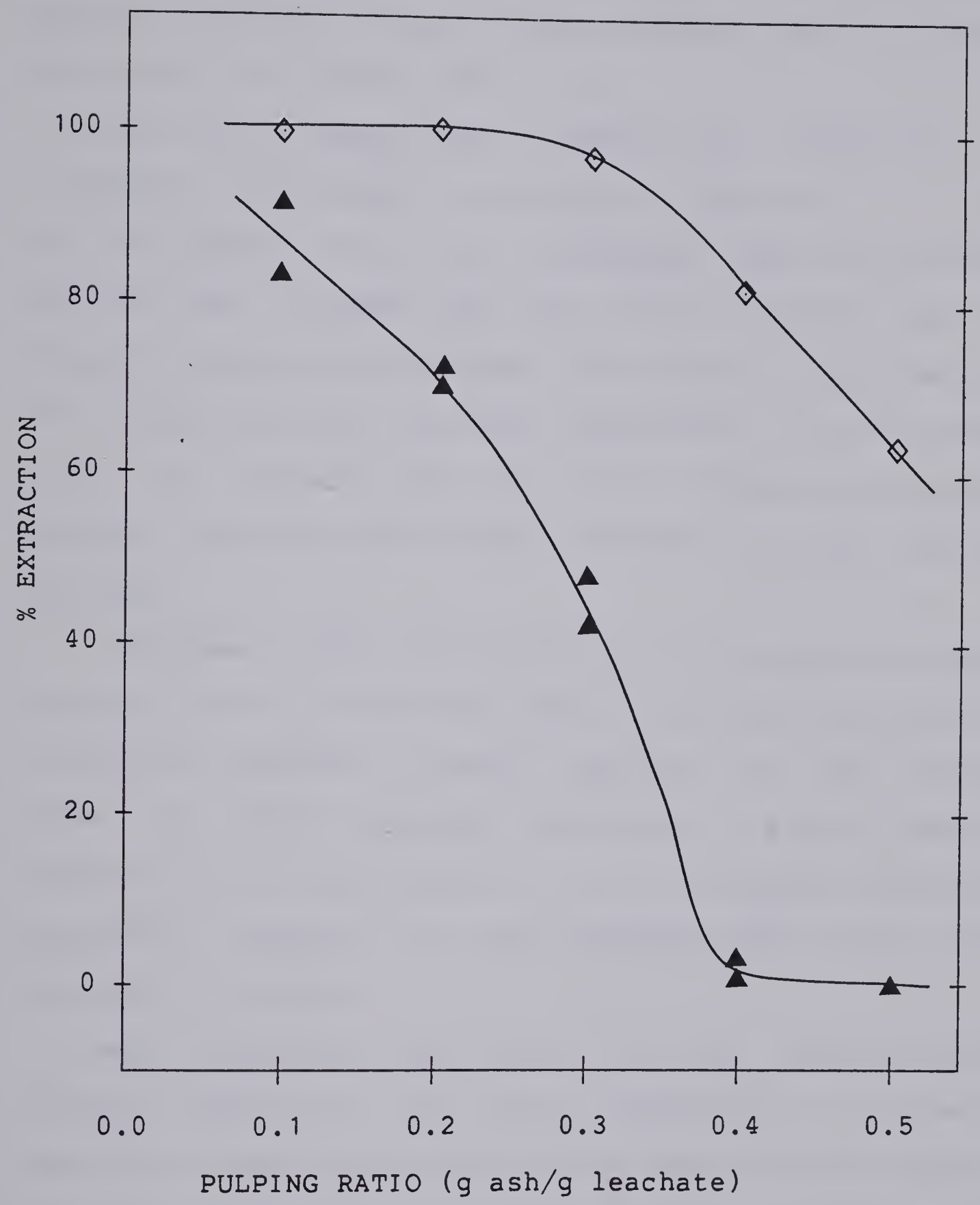

Figure 14. Extraction as a Function of Pulping Ratio in the Extraction of Laboratory Coke Ash With Sodium Carbonate.
▲ vanadium, ◇ sulfur.

the vanadium (assumed to be calcium vanadate) and calcium sulfate were extracted from the ash with the sodium carbonate solution through a base exchange reaction (Eq.[21] and Eq.[22]) (24, 105, 109).

$$Ca_3(VO_4)_2(s) + 3Na_2CO_3(aq) \rightarrow 2Na_3VO_4(aq) + 3CaCO_3(s)\downarrow \quad [21]$$

$$CaSO_4(s) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + CaCO_3(s)\downarrow \quad [22]$$

As the pulping ratio was increased, more of the sodium carbonate was consumed by the calcium sulfate and the vanadium extraction decreased. The absence of calcium oxide (or the hydrated form calcium hydroxide) in the leached solid, as indicated by the X-ray diffraction analysis, suggests calcium oxide also undergoes a base exchange reaction.

Ten grams of ash was combined with an excess[1] of sodium carbonate (10 g) and 25 ml water, the mixture boiled for 1 hr, and the leachate filtered. Analysis of the leachate showed an 80% vanadium extraction and a vanadium concentration in the leachate of 1.0 g/l vanadium pentoxide equivalent. Vanadium is thus extracted when excess sodium carbonate is present.

Any industrial application of this process appears unlikely because of the high consumption of carbonate leachate through the calcium sulfate base exchange reaction. Since the concentration of calcium sulfate in the ash is higher than the concentration of calcium oxide, the carbonate consumption by sulfate is even higher than the

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[1]The mole ratios of CO_3^{-2}:Ca = 1.12, CO_3^{-2}:SO_4^{-2} = 1.65.

consumption of sulfuric acid by calcium oxide in the acid extraction. Although the alkaline extraction process may be currently commercially unfeasible, several experiments were conducted to investigate the solvent extraction of vanadium from the carbonate leachate.

Equivalent weights of ash and sodium carbonate were combined with water (2.5 ml/g ash), the mixture boiled for 1 hr, and the leachate filtered without washing the filter cake. The pH of the leachate was about 12. The organic extractant used was 5 volume percent Aliquat 336 (Henkel Corporation, Minneapolis, Mn.) in kerosene (Gulf Canada Refinery, Edmonton) since Ritcey reported a high extraction of vanadium from pH 2 to 9 (83). The solvent extraction was conducted in a glass test tube placed in a temperature controlled water bath. A magnetic star spin bar was used to contact 3 ml of the organic with 10 ml of leachate at 60°C for 5 min, conditions typically used for the extraction of vanadium with Aliquat 336 (84, 85). A 5 ml sample of the aqueous phase was withdrawn, allowed to cool to room temperature, and a 2.0 ml sample taken for analysis. Evaporation of the leachate was minimized because of the short contact time. However, no vanadium was transfered to the organic phase presumably because the pH was too high. This is not unreasonable since sodium carbonate (1M) is a mild stripping agent and has been shown to extract 15% of the vanadium from an organic phase containing 4.5 g/l V_2O_5 (84). When the pH was adjusted to 7.2 with 2M sulfuric acid

prior to solvent extraction, 52.4% of the vanadium was extracted into the organic phase. However, a precipitate which formed during the pH adjustment settled at the aqueous/organic interface during the solvent extraction interfering with the phase separation.

The conclusion from the alkaline leach experiments is that it is technically possible to recover the vanadium from the ash by leaching with sodium carbonate and using solvent extraction to concentrate and purify the vanadium; however, the practicality is questionable. Excessive amounts of sodium carbonate are consumed through the precipitation of calcium carbonate, the preparation of the leachate for solvent extraction requires a pH adjustment, and an additional filtration step is required to remove the precipitate that forms during the pH adjustment.

V. CONCLUSION

The extraction of vanadium from commercially produced Suncor fly ash and laboratory-generated, low-sulfur-emission coke ash was examined.

With the Suncor fly ash, an overall vanadium recovery of 85% was obtained using a three part process: a sodium chloride roast to convert the vanadium in carbon-free fly ash to a water soluble form; a hot water leach; and the precipitation of vanadium from the leachate as ammonium metavanadate. This product would be suitable for thermal decomposition to vanadium pentoxide. The ammonium metavanadate product contained greater than 99% V_2O_5 equivalent, which is comparable to that currently produced industrially. The vanadium recovery efficiency was determined primarily by the roasting step. Roast conditions were optimized to minimize the numerous detrimental chemical reactions which could reduce the formation of water soluble vanadium compounds. Maximum recovery was obtained when carbon-free fly ash was roasted with 25% sodium chloride at 850 to 900° C for 4 to 6 hr under a low flow of dry air. Approximately 4% of the total vanadium was lost due to co-precipitation with impurities in a pH adjustment step prior to the precipitation of ammonium metavanadate. In an industrial scale-up, this loss could be reduced by recycling the precipitate to the fly ash feed.

Although the laboratory results are not sufficient to properly evalulate the economic feasibility, the overall

process is probably an economically feasible method of recovering vanadium from Suncor fly ash since similar processes are being used industrially to recover vanadium from uranium ore, magnetite and vanadiferous clays. With the vanadiferous clays, vanadium recovery as the sole product is economically feasible. A scale-up of the process using kilogram quantities of fly ash should provide sufficient data for a thorough economic evaluation.

The sodium chloride roast optimization identified the most important factors affecting the formation of water-soluble vanadium; however, a detailed examination of the effects of these factors was not possible due to time limitations. The effect of water vapor, roast gas flow rate, and oxygen partial pressure warrant further investigation. As well, the chemical reactions occuring between alkali salts and the various vanadium oxides require more study.

The use of the salt roast process for vanadium recovery from oil sands fly ash requires that the oil sands coke be burned. Since the coke contains 6 to 8% sulfur, government sulfur dioxide emission regulations have restricted the amount of coke that can be burned. Syncrude is able to burn only limited amounts of its coke production. Since the vanadium in the throughput of the Syncrude plant is not accessible to recovery by the salt roast process an alternate method of recovery was pursued.

Previous investigators showed that the addition of lime to bitumen prior to coking resulted in a coke with low

sulfur dioxide emission during combustion. Further, the vanadium and nickel could be readily extracted from the ash by acid leaching. The second part of this thesis concerned the investigation of techniques to further optimize the metals recovery by acid leaching and to convert the vanadium in the leachate to the primary product, vanadium pentoxide.

The vanadium concentration in the acid leachate produced using the original investigators' methods was too low to enable conversion to vanadium pentoxide by any economically feasible method. The solid to liquid ratio in the acid leachate was therefore optimized and the vanadium concentration in the leachate increased to 1.2 g/l V_2O_5, a concentration more amenable to recovery by solvent extraction. However, solvent extraction of the vanadium was unsuccessful because a gelatinous unfilterable precipitate formed during the pH adjustment of the leachate which was required prior to solvent extraction. All attempts to prevent the formation of the precipitate, to coagulate it, or to convert it to crystalline form failed.

As well as the difficulties noted above, excessive amounts of the acid leachate were consumed by the high concentration of unreacted calcium oxide remaining in the ash.

Since the recovery of vanadium with an acid leachate was not possible, vanadium recovery with a sodium carbonate leachate was investigated. However, similar problems were encountered with an equal lack of success.

The conclusion from these studies is that although addition of lime to bitumen allows the use of petroleum coke in combustion processes, the recovery of vanadium and nickel from the ash does not appear feasible.

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APPENDIX. Plackett-Burman Screening Designs

In the development of an industrial or laboratory process it is necessary to determine the factors which affect the overall outcome of the process and then to optimize the various factors to achieve the desired result. Such factors include temperature, time, or type of reactor. Statistical design experiments are one way in which to attain these objectives (100, 101).

The factorial design experiment is the most complete design and provides the most information with respect to the relative significance of each factor, optimum conditions, and factor interactions. However, the number of trials required is 2[exp(n)] where n is the number of factors to be tested. This design therefore becomes impractical as n becomes larger than four or five. For purposes of screening a large number of variables to determine those significant to the process, a screening design such as the Plackett-Burman screening design can be useful. Statistical analysis indicates the relative importance of the various factors and in the case of continuous variables indicates the direction of change of the variable which improved the outcome of the process. Information on the interaction of variables (changing the value of one factor changes the response characteristics of a second factor) or curvature (a

factor has an optimum effect at an intermediate value) is not obtainable, however. The more rigorous factorial design experiment is required.

The Plackett-Burman screening design is carried out as follows:

1. The experimenter selects the factors which may potentially affect the process;
2. The factors must be independent of each other. Time and temperature are independent whereas temperature and heating rate are not;
3. Each factor is assigned a high (+) or low (-) value. For example a high(+) and low(-) temperature are assigned for a quantitative variable such as temperature. For a qualitative factor such as reactor type, reactor 1(+) or reactor 2(-) are arbitrarily assigned to a high(+) or low(-) level. The spread between high and low variables should be as wide as is practical within the context of the process;
4. A design is chosen on the basis of the number of factors to be screened and the accuracy with which experimental error is to be measured. A 12, 20, or 28 trial design is chosen for a maximum of 11, 19, or 27 factors respectively. The trials are carried out in random order and the results for each trial used in the statistical calculations;
5. Statistical calculations. The statistical basis of experimental designs has been studied theoretically and

empirically for many years (98, 99). In principal, for a given variable results at the (+) level are statistically compared to the results at the (-) level above a background of experimental error. If the variable is having a significant effect on the outcome of the process, the results for the (+) level will be significantly different than for the (-) level. This is detected statistically by comparing the calculated FACTOR EFFECT to the value [MIN]. [MIN] is the standard deviation of the "FACTOR EFFECTS" of the unassigned factor columns. It takes into account experimental error and the observed "FACTOR EFFECT" in the absence of a variable. For a factor to be significant its absolute value must be equal to or larger than [MIN] according to the confidence level and the number of degrees of freedom used in calculating [MIN]. The sign of the FACTOR EFFECT indicates whether it was the + level or the - level which produced the better result;

6. Normally three to five factors are found to have a significant effect on a process, other factors having only a minor effect.

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